Chapter 4.1

Synthesis, Antihyperglycemic Activity and Photophysical Properties of Functionalized Fluorenes and Fluorenones
Chapter 4.1: Synthesis, Antihyperglycemic Activity and Photophysical Properties of functionalized Fluorenes and Fluorenones.

4.1.1 Introduction

Development of new sensitive analytical techniques i.e. labeling and biomarkers not only helps in better understanding of substrate and protein interactions required for \textit{in vitro} and \textit{in vivo} studies but also it opens a new era of drug development approach.\textsuperscript{1} However, in recent years, detections based on fluorescence techniques have received special attention and notable progress has been made in the synthesis of new fluorophores. Use of organic molecules as fluorophores in labeling experiments is becoming a hot research topic and it is not only limited to labeling experiments but also a newer field of organic semiconductors has been emerged in the last decade which shows their importance in material chemistry as well.\textsuperscript{2} The main advantage associated with the organic molecules is their easier preparation, higher quantum yield, high photo- and thermal stability and availability of full range spectrum (UV-near IR). Our main aim was synthesis and characterization of new fluorescent organic molecules and evaluation of their photophysical properties. An extensive literature search revealed several organic fluorophores such as 3-oxo-3\textit{H}-benzopyrans I (coumarins),\textsuperscript{3,4} Oxobenzo[\textit{f}]benzopyrans II,\textsuperscript{5} Benzofurans III,\textsuperscript{6} Naphthofurans IV,\textsuperscript{7} Benzooxadiazoles\textsuperscript{8} V, Naphthalene\textsuperscript{9} VI and Fluorene VII based scaffolds which shows absorption and emission in the range of 400-500nm and fluoresceins,\textsuperscript{10} rhodamines\textsuperscript{11} and their analogs for beyond 500nm (Figure 1). Due to high thermal stability and high quantum efficiencies associated with fluorene scaffolds we choose donor-acceptor fluorene and its related compounds as new fluorescent probes and explored their synthesis, antihyperglycemic activity and photophysical properties by UV-vis and fluorescence spectroscopy, thermal stability by TGA and DSC experiments and successfully demonstrated their potential use as organic light emitting materials.

First section of this chapter deals with their synthesis, spectroscopic characterization and antihyperglycemic activity of fluorenes and fluorenones and second section deals with their photophysical and optical properties.

The demand for fluorene and fluorenone systems functionalized with electron-donor or electron-acceptor substituents in both synthetic and medicinal perspectives has increased dramatically during the past few decades. Numerous synthetic fluorenes and fluorenones
have been reported as antifertility (XII), as antimalarial (XIII) (lumefantrine), as aldose reductase inhibitors (XIV), estrogen receptor agonists. Besides their great diversity in natural products and pharmaceuticals these compounds are fascinating and challenging research objects in material sciences. Owing to their unique photophysical properties (Figure 1; VIII-XI), these scaffolds have proven their potential for the preparation of organic light emitting diodes.

Numerous synthetic methodologies are available for the synthesis of fluorenes and fluorenones. In general, palladium-catalyzed Suzuki-Miyaura coupling protocol has been used to prepare a wide array of fluorenes, spirofluorenes and related scaffolds. Corey et al. reported the synthesis of fluorenes from 2-chloro-p-xylene by treating it with a 1:1 mixture of lithium piperidide, phenyllithium and ethyltrifluoroacetate. Larock et al. reported the synthesis of 9-alkylidienes-9H-fluorenes by treating aryl iodides with 1-aryl-1-alkynes in the presence of palladium-catalyst. The general palladium-free approaches for fluoren-9-ones include Fridel-Craft ring closer of biaryl carboxylic acid derivatives, intramolecular [4+2] cycloaddition reactions of conjugated enynes, oxidation of fluorenes and remote metallation of 2-biphenylcarboxamides or 2-biphenyloxazolines. Fluorene-9-ones have been recently synthesized by the palladium-catalyzed cyclization of iodobenzophenones.
Despite the wide synthetic potential of these metal-assisted cross-coupling reactions, they suffer from the requirements for expensive organometallic reagents/catalysts, harsh reaction conditions and undesired byproducts. Thus, there exists a need to develop an expeditious route for the synthesis of functionalized fluorenes and fluorenones, which do not require specialized reagents or catalysts and could offer economical general route with flexibility of introducing the electron-donor or electron-acceptor groups in their molecular architecture.

We demonstrate a new protocol for the synthesis of functionalized fluorenes and fluorenones through ring transformation reactions of 2H-pyran-2-ones with 1-indanone or 2-indanone in high yields, and unprecedented aerial oxidation of fluorenes to fluorenones under basic conditions at room temperature. The potential of the procedure lies in the creation of an aromatic ring utilizing a simple transformation strategy without using an expensive organometallic reagent or a catalyst. Synthesized compounds have been evaluated for anti-hyperglycemic activity.

![Figure 2. Structure of prototypes (XIV - XIX).](image)

### 4.1.2 Chemistry

2H-Pyran-2-ones prepared from α-oxo-ketene-S,S-acetal\(^{27}\) (1) have promising structural topology as useful substrates for ring transformation reactions, flexible substitution pattern and the presence of a good leaving alkylsulfanyl group for generating molecular diversity.\(^{28}\) It has been reported\(^ {29}\) that α-pyranone ring can be converted to a benzene ring under mild basic conditions. Recently, Goel et al exploited the lactone methodology to synthesize various functionalized Biaryls,\(^ {30}\) functionalized donor-acceptor quateraryls as potential candidates for small molecule blue organic light emitting diodes.\(^ {31}\)

#### 4.1.2.1 Synthesis of 4-aryl-2-(amin-1-yl)-9H-fluorene-1-carbonitriles (3a-k) and 1-aryl-3-(amin-1-yl)-9H-fluorene-4-carbonitrile (6a-c): Our approach to preparing functionalized fluorenes (3a-k) was based on the ring transformation of 6-aryl-3-cyano-4-sec.amino-2H-pyran-2-ones (1a-k) by using 2-indanone 2 as a carbanion source. The 2H-pyran-2-ones (1a-
k) used as a parent precursors were prepared by the reaction of methyl 2-cyano-3,3-dimethylsulfanylacrylate\textsuperscript{28} with aliphatic ketones under alkaline conditions in high yields.

Lactones, (1a-k) have three electrophilic centres; C-2, C-4 and C-6 in which the latter position is highly reactive towards nucleophiles due to the extended conjugation and the presence of an electron withdrawing substituent at position 3 of the pyran ring. The functionalized fluorene derivatives (3a-k) were synthesized by stirring 1 eq of 2\textit{H}-pyran-2-ones (1a-k), 1.2 eq of 2-indanone and 2 eq of NaH in dry THF for 5-10 min. at room temperature under nitrogen atmosphere (Scheme 1). The reaction was monitored by TLC and thereafter reaction mixture was concentrated under reduced pressure and then poured into ice water, finally neutralized with dilute HCl. The crude product thus obtained was purified by silica gel column chromatography using 1% ethylacetate in hexane as eluent.

![Scheme 1. Mechanism involved in the synthesis of 4-aryl-2-(amin-1-yl)-9\textit{H}-fluorene-1-carbonitriles (3a-k).](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>N</th>
<th>Reaction time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>4-BrC\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>5</td>
<td>88</td>
</tr>
<tr>
<td>3b</td>
<td>4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>&lt;5</td>
<td>79</td>
</tr>
<tr>
<td>3c</td>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>piperidine</td>
<td>&lt;5</td>
<td>89</td>
</tr>
<tr>
<td>3d</td>
<td>4-FC\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>6</td>
<td>81</td>
</tr>
<tr>
<td>3e</td>
<td>4-OMeC\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>&lt;5</td>
<td>82</td>
</tr>
<tr>
<td>3f</td>
<td>thiophene-2-yl</td>
<td>piperidine</td>
<td>5</td>
<td>84</td>
</tr>
<tr>
<td>3g</td>
<td>Furan-2-yl</td>
<td>piperidine</td>
<td>6</td>
<td>83</td>
</tr>
<tr>
<td>3h</td>
<td>4-ClC\textsubscript{6}H\textsubscript{4}</td>
<td>pyrrolidine</td>
<td>&lt;5</td>
<td>76</td>
</tr>
<tr>
<td>3i</td>
<td>4-CH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</td>
<td>pyrrolidine</td>
<td>7</td>
<td>72</td>
</tr>
<tr>
<td>3j</td>
<td>4-COCH\textsubscript{3}C\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>6</td>
<td>76</td>
</tr>
<tr>
<td>3k</td>
<td>4-pyrrole-C\textsubscript{6}H\textsubscript{4}</td>
<td>piperidine</td>
<td>&lt;5</td>
<td>79</td>
</tr>
</tbody>
</table>

The transformation of 2\textit{H}-pyran-2-ones into fluorene derivatives is possibly initiated by attack of the 2-indanone carbanion at position C-6 of lactone 1, followed by intra-
molecular cyclization and elimination of carbon dioxide to yield 3a-k. All of the synthesized compounds were characterized by their spectroscopic analysis.

IR spectrum of compound 3a showed a band at 2211 cm\(^{-1}\) due CN group. The \(^1\)H NMR spectrum of compound 3a showed three multiplets at \(\delta 1.80-1.85\) ppm, 1.80-1.85 ppm and 3.20-3.24 ppm for 2H, 4H and 4H assigned to piperidine protons, respectively. A singlet appeared at \(\delta 4.07\) ppm for 2H was assigned to methylene group. One singlet and one doublet at 6.71 ppm and 6.83 ppm each for 1H, two triplets at 7.05 ppm & 7.18 ppm each for 1H, three doublets at 7.31 ppm, 7.48 ppm and 7.63 ppm for 2H, 1H and 2H respectively, were assigned to aromatic protons (figure 3). Mass spectrum (ESIMS) at \(m/z\) 430 (M\(^{+2}\)) confirms the structure as 4-(4-bromophenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3a).

![Figure 3. \(^1\)H and \(^{13}\)C NMR spectra of 4-(4-bromophenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3a).](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Reaction time (min.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>thiophene-2-yl</td>
<td>piperidine</td>
<td>6</td>
</tr>
<tr>
<td>6b</td>
<td>4-FC(_6)H(_4)</td>
<td>piperidine</td>
<td>7</td>
</tr>
<tr>
<td>6c</td>
<td>2,5-dimethylfuryl-3yl</td>
<td>piperidine</td>
<td>5</td>
</tr>
</tbody>
</table>

Scheme 2.

Our approach to preparing 1,3,4 substituted fluorene derivatives (6a-c) was based on the ring transformation of 6-aryl-3-cyano-4-sec.amino-2H-pyran-2-ones (4a-c) by using
indanone-1 (5) as a carbanion source. The 2H-pyran-2-ones (4a-c) used as a parent precursors were prepared using same protocol as described above. The synthesis of substituted 1-aryl-3-(amin-1-yl)-9H-fluorene-4-carbonitriles (6a-c) was achieved by stirring a 1:1.2 molar mixture of 2H-pyran-2-ones (4a-c), indanone-1 (5) and 2 molar NaH in dry THF for 5-7 min. under nitrogen atmosphere, at room temperature (Scheme 2). The mechanism for the formation of substituted 1-aryl-3-(amin-1-yl)-9H-fluorene-4-carbonitriles (5a-c) is similar to the formation of substituted fluorene derivatives 3a-k (Scheme 1).

All the synthesized compounds were characterized by their spectroscopic analysis. The $^1$H NMR spectrum of compound 6b showed three multiplets at $\delta$ 1.65-1.67, 1.87-1.90 and 3.21-3.24 ppm for 2H, 4H and 4H assigned to piperdine. A singlet appeared at $\delta$ 3.80 ppm for 2H was assigned to one methylene group protons. A singlet appeared at $\delta$ 6.83 ppm for 1H and a set of multiplets at $\delta$ 7.13-7.21, 7.34-7.38 and 7.43-7.47 ppm for 2H, 1H and 4H, one doublet at 8.55 ppm for 1H were assigned to aromatic protons. IR spectrum showed peak at 2220 cm$^{-1}$ due to CN group. Mass spectrum (ESIMS) at m/z 368 confirmed the structure of 6b as 1-(4-fluorophenyl)-3-(piperidin-1-yl)-9H-fluorene-4-carbonitrile.

4.1.2.2 Synthesis of Fluorenones from their corresponding Fluorenes: Direct oxidation of alkyl arenes to the corresponding carbonyl compounds is an important transformation in organic synthesis because an oxygen atom can be introduced into organic substrate. For these transformations a stoichiometric amount of an oxidant such as manganese dioxide, chromic acid and selenium dioxide has been employed traditionally.32 Numerous homogeneous and heterogeneous catalyst have been used for direct oxidation of alkyl arenes to the corresponding carbonyl compounds like ruthenium-catalysed oxidation of alkanes with tert-butyl hydroperoxide and peracetic acid,33 KMnO$_4$-supported on montmorillonite K10 in dry media.34 Badri et. al. reported a new catalyst 3,6-bis(triphenylphosphonium)cyclohexene peroxodisulphate (BTPCP) for the oxidation of benzylic compounds.35 Einhorn and co-workers reported a new catalyst N-hydroxy-3,4,5,6-tetraphenylphthalimide (NHTPPI)/CuCl for the oxidation of alkyl arenes under mild reaction condition with low catalyst loading.36 The methods for the oxidation of fluorenes require either specially designed organometallic-catalyst or harsh reaction conditions. We developed an unusual new protocol for the preparation of fluorenones from the corresponding fluorenes at room temperature without using any organometallic reagent or catalyst.

While, we were synthesizing fluorenes under basic conditions (NaH in THF) we found that prolonged stirring of the reaction mixture of 1/4 and indanones resulted in the conversion of fluorenes into fluorenones together with decomposed byproducts. Therefore a
separate reaction of fluorene with NaH in presence of air was carried out which resulted in the formation of fluorenone as a sole product in just 5-10 min. This aerial oxidation of fluorenes into fluorenones under basic condition without using any catalyst is quiet unusual and has not been reported prior to this study.

To generalize the protocol we carried out the oxidation of fluorene, 2-acetyl fluorene and anthrone, interestingly these compounds were converted into their corresponding carbonyl compounds (Table 1) in excellent yields.

![Chemical structure](image)

**Table 2 Fluorenes and their Fluorenones**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Fluorene</th>
<th>Fluorenone</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Fluorene structure" /></td>
<td><img src="image" alt="Fluorenone structure" /></td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Acetyl derivative" /></td>
<td><img src="image" alt="Acetyl fluorenone" /></td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Anthrone" /></td>
<td><img src="image" alt="Anthrone fluorenone" /></td>
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<tr>
<td>5</td>
<td><img src="image" alt="Fluorene 5" /></td>
<td><img src="image" alt="Fluorenone 5" /></td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Fluorene 6" /></td>
<td><img src="image" alt="Fluorenone 6" /></td>
<td>88</td>
</tr>
</tbody>
</table>
A typical procedure involves simple stirring of fluorenes with NaH in THF for 5-8 min. The excess THF was removed under vacuum and thereafter reaction mixture was poured into cold water and neutralized with dil. HCl, the crude product obtained was filtered and purified on silica gel column using 2% ethylacetate in hexane as eluent. To generalize our protocol we also carried out the oxidation of unsubstituted fluorene, 2-acetyl fluorene and
anthrone and they were easily converted into their corresponding carbonyl compounds (Table 1) in excellent yields.

Scheme 3. Plausible mechanism for the conversion of fluorene into fluorenone

The oxidation of fluorene is possibly initiated by the abstraction of a proton in the presence of a base, followed by reaction with atmospheric oxygen to form a peroxy anion intermediate B. This intermediate B on elimination of hydroxide ion afforded fluorenone in excellent yields (Scheme 3). All synthesized compounds were characterized by spectroscopic analysis.

Figure 4. $^1$H NMR of as 9-oxo-3-(piperidin-1-yl)-1-(thiophen-2-yl)-9H-fluorene-4-carbonitrile 11a.

IR spectrum of the compound 11a showed peaks at 1703 cm$^{-1}$ due to CO functionality and at 2218 cm$^{-1}$ due to a CN group. $^1$H NMR spectrum of compound 11a showed three multiplets at $\delta$ 1.66-1.75 ppm for 2H, 1.81-1.90 ppm for 4H and 3.38-3.44 ppm for 4H assigned to piperidine protons. Three multiplets at $\delta$ 7.15-7.20, 7.47-7.50 and 7.82-7.86 ppm each for 1H were assigned to thiophene group. One singlet at $\delta$ 6.88 ppm for 1H.
and remaining four aromatic protons splits into two multiplets at 7.39-7.46 ppm and 7.54-7.62 ppm and two doublets at δ 7.68 ppm and 8.38 ppm each for 1H (figure 4). Mass spectrum (ESIMS) at m/z 371 (M⁺+1) confirms the structure as 9-oxo-3-(piperidin-1-yl)-1-(thiophen-2-yl)-9H-fluorene-4-carbonitrile 11a.

4.1.2.3 Optimization for oxidation of Donor-Acceptor fluorenes into fluorenones:
Fluorene (3a) taken as model compound was treated with various bases to optimise the protocol of aerial oxidation. A list of bases used together with the yield of fluorenone is listed in table 2. Typical procedure used in all cases was same as described earlier. From table 1 it is evident that the best condition is NaH.

**Table 1.** List of bases used for the conversion of Fluorenes into Fluorenones

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Base</th>
<th>Equivalent</th>
<th>Time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOH</td>
<td>1.2</td>
<td>5min.</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>Ba(OH)₂</td>
<td>1.2</td>
<td>30min.</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>NaOH</td>
<td>1.2</td>
<td>15min.</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>LiOH</td>
<td>1.2</td>
<td>1h</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>NaH</td>
<td>1.2</td>
<td>&lt;5min</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>t-BuOK</td>
<td>1.2</td>
<td>5min.</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>n-BuLi</td>
<td>1.2</td>
<td>1.5hr</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>NaOMe</td>
<td>1.2</td>
<td>1hr</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Na₂CO₃</td>
<td>1.2-3</td>
<td>1hr</td>
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</tr>
<tr>
<td>10</td>
<td>K₂CO₃</td>
<td>1</td>
<td>2hr</td>
<td>15</td>
</tr>
<tr>
<td>11</td>
<td>Cs₂CO₃</td>
<td>3</td>
<td>30min.</td>
<td>58</td>
</tr>
<tr>
<td>12</td>
<td>NaHCO₃</td>
<td>1</td>
<td>1hr</td>
<td>0</td>
</tr>
</tbody>
</table>

**Scheme 4.** Synthetic Scheme showing the formation of unknown product (12a-c).
1-cyano-2-amino-fluorene (3a) when treated with KOH, we got flurenone (10c) and one unknown product 12a (Scheme 4). The unknown product was characterized using IR, Mass, $^1$H NMR, $^{13}$C NMR and X-ray analysis.

$^1$H NMR spectrum of compound 12a showed a set of three multiplets at $\delta$ 1.56-1.60 ppm, 1.67-1.78 ppm and 2.80-2.89 ppm for 2H, 4H and 4H respectively, for piperidine protons. An appearance of broad singlet at $\delta$ 5.99 was assigned to NH$_2$ group. One singlet at $\delta$ 6.71 ppm for 1H and four multiplets at 6.76-6.85 ppm for 1H, 7.10-7.18 ppm for 2H, 7.30-7.35 ppm for 2H and 7.55-7.61 ppm for 3H were assigned to aromatic protons (figure 5). Disappearance of CN peak in IR spectrum and presence of additional peaks at 1671 (CO) for carbonyl and 3365 & 3473 cm$^{-1}$ due to NH$_2$ group. Molecular ion peak at $m/z$ 433 (M$^+$+1) together with HRMS confirms the structures as 1-amino-4-(4-bromophenyl)-2-(piperidin-1-yl)-9H-fluoren-9-one 12a. Finally structure of 12a was confirmed unambiguously by X-ray Crystal structure analysis.

![Figure 5. $^1$H NMR spectrum of 1-amino-4-(4-bromophenyl)-2-(piperidin-1-yl)-9H-fluoren-9-one 12a.](image)

4.1.2.3.1 X-Ray Crystal structure analysis of compound 12a

The conformation of the compound (12a) along with atomic numbering scheme is shown in Fig. 6. The molecule consists of a fused three ring system (D/A/C) to which amino group is substituted at C1, piperidine ring at C2 and bromophenyl ring attached at C4 positions. The least square mean plane angle between the ring E and fused rings D/A/C is 54.45°.
The structural analysis of the compound shows that molecule crystallized in monoclinic pattern with space group \( \text{C2/c} \). The structural analysis reveals the presence of intermolecular \( \pi-\pi \), C-H-\( \pi \) interaction. There are two intramolecular N-H...O and N-H...N type H-bonding interactions with parameters \([H2A...O1 = 2.34\text{Å}, <C2-H2A-O1 = 128^\circ, C2-O1 = 2.9953 \text{Å}; H2B...N1 = 2.42\text{Å}, <N2-H2B-N1 = 104^\circ, N2-N1 = 2.759 \text{Å}]\). The crystal packing analysis further reveals the presence of intermolecular N-H...O type \([H2...O1 = 2.483 \text{Å}, <C2-H2-O1 = 122^\circ, C2-O1 = 3.033 \text{Å}]\) and C-H...O type interactions \([H19...O1 = 2.55 \text{Å}, <C19-H19-O1 = 159^\circ, C19-O1 = 3.435\text{Å}]\), (symmetry codes: 1-x, 1-y, -z). Packing also reveals the presence of C17-Br1... \( \pi \) short contact with the neighbouring \( \pi \) bond between C7 and C8 atoms of ring D.

Figure 6: ORTEP diagram of compound 12a with atomic numbering scheme.

Figure 7: Packing diagram showing the existence of intermolecular \( \pi-\pi \), C-H-\( O \) and N-H...O interactions

Figure 8: Packing diagram showing the existence of intermolecular bromine...\( \pi \) and intramolecular N-H...O and N-H...N interactions
4.1.2.4 Factors influencing unusual conversion of 3(a-c) to 12(a-c): In order to understand the mechanism for the unusual conversion of 1-cyano-2-amino-4-arylfluorene (3a-c) into 1,2-diamino-4-arylfluorene (12a-c), we carried out systematic studies by changing the substituents onto the fluorene backbone.

4.1.2.4.1 Effect of substituent at position 2 & 4: In order to understand the effect of substituents at position 2 & 4 of fluorene (3a), a reaction was tried with 1-cyanofluorene 13, which was easily prepared from 1-fluorenecarboxylic acid by known literature method.\(^{37}\) However, in this case, we got exclusively 1-cyanofluorenone (14) as a sole product (Scheme 5). This clearly indicates that substituent at position 2 & 4 of fluorene (3a) playing a major part during the course of unusual oxidation reaction.

\[
\text{Scheme 5.}
\]

4.1.2.4.1.1 Effect of donor substituent at position 2: To examine the effect of amines, at position 2 of fluorene (3) it was replaced by two groups, first with methylsulfanyl group and second with N,N-dimethylamine. In case of methylsulfanyl (17a,b), 2-(methylthio)-9-oxo-4-aryl-9H-fluorene-1-carbonitrile (18a-b) was formed as a sole product under the similar reaction condition as described earlier (Scheme 6). In case of N,N-dimethylamine (20), the reaction proceeds smoothly and we got both products (21 & 22) (Scheme 7). These studies suggest that on increasing the electrophilicity at position 2 of fluorene by replacing methylsulfanyl group with N,N-dimethylamino group favours the reaction, which shows the requirement of strong donor group at position 2 of fluorene.

4.1.2.4.1.1.1 Synthesis of 4-aryl-2-(methylthio)-9H-fluorene-1-carbonitrile (17a-b) and 2-(methylthio)-9-oxo-4-aryl-9H-fluorene-1-carbonitrile (18a-b): Our approach to preparing 4-aryl-2-(methylthio)-9H-fluorene-1-carbonitrile (17a-b) was based on the ring transformation of 6-aryl-3-cyano-4-methylsulfanyl-2H-pyran-2-ones (16a-b) by using 2-indanone (2) as a carbanion source. The 2H-pyran-2-ones (16a-b) used as a parent
precursors were prepared conveniently using same protocol as described in scheme 1. The synthesis of substituted 4-aryl-2-(methylthio)-9H-fluorene-1-carbonitrile (17a-b) was achieved by stirring a 1:1.2 molar mixture of 2H-pyran-2-ones (16a-b), 2-indanone (2) and 2 molar NaH in dry THF for 5-8 min. under N₂ atmosphere, at room temperature (Scheme 6). The mechanism for the formation of substituted 4-aryl-2-(methylthio)-9H-fluorene-1-carbonitrile (17a-b) is similar to the formation of fluorene derivatives 3a-k. An equimolar mixture of 4-aryl-2-(methylthio)-9H-fluorene-1-carbonitrile (17a-b) and KOH in DMF was stirred for 5 min. afforded 4-aryl-2-(methylthio)-9-oxo-9H-fluorene-1-carbonitrile 18a-b (Scheme 6). All the synthesized compounds were characterized by spectroscopic analysis. Figure 9 and figure 10 shows the ¹H NMR of 17b and 18b respectively.

\[ \text{Scheme 6. Effect of methylsulfanyl group at position 2} \]

¹H NMR spectrum of 17b showed two singlets at δ 2.60 ppm for SCH₃ protons and 4.09 ppm for one methylene protons. Two doublets at δ 6.90 ppm for 1H and 7.39 ppm for 2H and three multiplets at 7.10-7.16 ppm for 2H, 7.28-7.32 ppm for 1H and 7.49-7.55 ppm for 3H were assigned to aromatic protons (figure 9). IR spectrum showed peak at 1671 cm⁻¹ due to carbonyl group. Molecular ion peak at m/z 347 (M⁺+1) confirms the structures as 4-(4-chlorophenyl)-2-(methylthio)-9H-fluorene-1-carbonitrile 17b.

¹H NMR spectrum of 18b showed one singlet at δ 2.60 ppm for SCH₃ protons. One singlet at δ 7.17 ppm and two doublets at 7.44 and 7.39 ppm each for 2H and three multiplets at 6.68-6.73 ppm for 1H, 7.23-7.29 ppm for 2H and 7.65-7.70 ppm for 1H were assigned to aromatic protons. IR spectrum showed peak at 1716 and 2224 cm⁻¹ due to carbonyl and cyano group. Molecular ion peak at m/z 347 (M⁺+1) confirms the structures as 4-(4-chlorophenyl)-2-(methylthio)-9-oxo-9H-fluorene-1-carbonitrile 18b (figure 10).
Figure 9. $^1$H NMR spectrum of 4-(4-chlorophenyl)-2-(methylthio)-9H-fluorene-1-carbonitrile (17b).

Figure 10. $^1$H NMR spectrum of 4-(4-chlorophenyl)-2-(methylthio)-9-oxo-9H-fluorene-1-carbonitrile (18b).

4.1.2.4.1.1.2 Synthesis of 1-amino-4-(4-bromophenyl)-2-(dimethylamino)-9H-fluoren-9-one (21) & 4-(4-bromophenyl)-2-(dimethylamino)-9-oxo-9H-fluorene-1-carbonitrile
Our Approach to preparing 1-amino-4-(4-bromophenyl)-2-(dimethylamino)-9H-fluoren-9-one 21 was based on the oxidation of 4-(4-bromophenyl)-2-(dimethylamino)-9H-fluorene-1-carbonitrile (20) as shown in Scheme 7. Compound 20 was easily prepared by the ring transformation of 6-(4-bromophenyl)-4-(dimethylamino)-2-oxo-2H-pyran-3-carbonitrile (19) using 2-indanone (2) as a source of carbanion. The required precursor 6-(4-bromophenyl)-4-(dimethylamino)-2-oxo-2H-pyran-3-carbonitrile 19 was synthesized by replacing the methylsulfanyl group of 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2H-pyran-3-carbonitrile 16a, by refluxing it with N,N-dimethylamine in THF. Thus synthesis of 4-(4-bromophenyl)-2-(dimethylamino)-9H-fluorene-1-carbonitrile 20 was acheived by stirring a 1:1.2 eq. mixture of 6-(4-bromophenyl)-4-(dimethylamino)-2-oxo-2H-pyran-3-carbonitrile 19, 2 eq. NaH in dry THF under N₂ atmosphere at room temperature. Finally the synthesis of compound 21 & 22 was achieved by stirring an equimolar mixture of 4-(4-bromophenyl)-2-(dimethylamino)-9H-fluorene-1-carbonitrile 20 and KOH in DMF for 10min. All the synthesized compounds were characterized using spectroscopic analysis.

Scheme 7. Effect of N,N-dimethylamine group at position 2

4.1.2.4.1.2 Effect of substituent at position 4: In order to study the role of aryl substituent at position 4 of fluorene (3a), aryl ring was replaced with alkyl substituent such as isopropyl (Scheme 8). The synthesis of fluorene with alkyl substituent at position 4, was achieved through a ring transformation reaction using 6-isopropyl-2-oxo-4-(piperidin-1-yl)-2H-pyran-3-carbonitrile 23 and 2-indanone 2 as a carbanion source. Thus stirring a (1:1.2) molar mixture of 6-isopropyl-2-oxo-4-(piperidin-1-yl)-2H-pyran-3-carbonitrile (23), 2-indanone
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(2) and 2 molar NaH in dry THF, afforded 4-isopropyl-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile 24 (Scheme 7). Then the synthesized alkyl fluorene was stirred with KOH in DMF and as expected we got both products 1-amino-4-isopropyl-2-(piperidin-1-yl)-9H-fluoren-9-one (25) & 4-isopropyl-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (26) in good yields. It shows that the reaction will proceed smoothly whether the substituent present at position 4 is aryl or alkyl. Hence substituent present at this position has not much effect on the reaction mechanism.

Scheme 8 Effect of substituent at position 4

In order to explore the synthetic utility, this unusual transformation was further extended to 1-aryl-3-amino-4-cyano-fluorenes (6), but reaction failed in this case (Scheme 9), which indicates that the presence of a cyano group at position 1 and amino group at position 2 play an important role in such an unusual conversion.

Scheme 9.

4.1.2.5 Conclusion

In conclusion we developed a novel and one pot approach for the synthesis of fluorene and successfully coverted fluorenes into their corresponding fluorenones via an unprecedented aerial oxidation. We optimized our protocol using a variety of bases and a
systematic study of substituents at position 2 & 4 of fluorene (3a) for the unusual transformation of a cyano group into an amino group in presence of KOH.

4.1.3 Results and Discussion

4.1.3.1 Evaluation of Antihyperglycemic Activity

*In vitro* glucose-6-phosphatase, glycogen phosphorylase and α-glycosidase activity of most of the compounds at 100 µM concentration were examined as described in experimental section of Chapter 4. The compounds showed moderate inhibitory activity.

Table 3. *In vitro* antihyperglycemic activity of compounds 3a-i, 6a-b

<table>
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<td>7.7</td>
<td>+0.6</td>
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<tr>
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<td>1.5</td>
</tr>
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<td>38.4</td>
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<td>+2.5</td>
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*Compounds were evaluated at 100 µM concentration.

4.1.4 Experimental Section

**General procedure for the synthesis of compounds 3a-k:** A mixture of 6-aryl-4-sec. amino-2-oxo-2H-pyran-3-carbonitrile 1a-k (1 mmol), 2-indanone 2 (1.2 mmol) and NaH (2 mmol) in dry THF (5 mL) in N₂ was stirred at room temperature for 5-10 min. The excess THF was removed under vacuum and thereafter reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl. The solid thus obtained was filtered and purified on a silica gel column using chloroform-hexane (1:5) as eluent.

**4-(4-Bromophenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3a)**

White solid; yield 88%; mp 210-212 °C; ESI-MS 430(M+2); IR (KBr) 2211 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.57-1.66 (m, 2H, CH₂), 1.78-1.85 (m, 4H, 2CH₂), 3.21-3.28 (m, 4H, 2CH₂), 4.07 (s, 2H, CH₂), 6.76 (s, 1H, ArH), 6.87 (d, J = 7.8Hz, 1H, ArH), 7.09 (t, J = 7.8Hz, 1H, ArH), 7.22 (t, J = 7.8Hz, 1H, ArH), 7.33 (d, J = 8.4Hz, 2H, ArH), 7.52 (d, J = 7.8Hz, 1H, ArH), 7.64 (d, J = 8.4Hz, 2H, ArH); ¹³C NMR (75MHz, CDCl₃) δ 22.81, 24.88, 127
2-(Piperidin-1-yl)-4-p-tolyi-9H-fluorene-1-carbonitrile (3b)
White solid; yield 79%; mp 162-164 °C; ESIMS 365 (M⁺+1); IR (KBr) 2213 cm⁻¹ (CN); ¹H NMR (200 MHz, CDCl₃) δ 1.55-1.64 (m, 2H, CH₂), 1.79-1.81 (m, 4H, 2CH₂), 2.48 (s, 3H, CH₃), 3.19-3.26 (m, 4H, 2CH₂), 4.10 (s, 2H, CH₂), 6.80 (s, 1H, ArH), 6.91 (d, J = 7.7 Hz, 1H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 7.15-7.24 (m, 1H, ArH), 7.31-7.38 (m, 4H, ArH), 7.50 (d, J = 7.3 Hz, 2H, ArH); ¹³C NMR (50MHz, CDCl₃) δ 21.79, 24.55, 26.62, 30.13, 37.68, 53.81, 101.95, 117.81, 119.72, 122.52, 125.18, 126.66, 126.96, 128.90, 129.75, 133.04, 137.57, 138.44, 141.00, 142.61, 142.79, 150.69, 155.30; HRMS calcd. for C₂₆H₂₄N₂ 364.1940 Found 364.1936.

4-Phenyl-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3c)
White solid; yield 89%; mp 140-141 °C; ESIMS 351 (M⁺+1); IR (KBr) 2219 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.62-1.75 (m, 2H, CH₂), 1.79-1.91 (m, 4H, 2CH₂), 3.27-3.32 (m, 4H, 2CH₂), 4.10 (s, 2H, CH₂), 6.86-6.91 (m, 2H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.22 (t, J = 7.6 Hz, 1H, ArH), 7.45-7.61 (m, 6H, ArH); ¹³C NMR (75.53 MHz, CDCl₃): δ 22.89, 24.96, 36.00, 52.15, 100.45, 116.08, 117.93, 120.78, 123.54, 125.06, 125.34, 126.97, 127.35, 127.42, 131.32, 138.85, 139.20, 140.94, 141.01, 149.06, 153.62; HRMS (ESIMS) calcd. for C₂₅H₂₂N₂ 351.1861 Found 351.1821.

4-(4-Fluorophenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3d)
White solid; yield 81%; mp 130-132 °C; ESIMS 369 (M⁺+1); IR (KBr) 2216 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.59-1.67 (m, 2H, CH₂), 1.78-1.91 (m, 4H, 2CH₂), 3.21-3.27 (m, 4H, 2CH₂), 4.07 (s, 2H, CH₂), 6.77 (s, 1H, ArH), 6.82 (d, J = 7.8Hz, 1H, ArH), 7.07 (t, J = 7.5Hz, 1H, ArH), 7.16-7.24 (m, 3H, ArH), 7.38-7.45 (m, 2H, ArH), 7.51 (d, J = 7.2Hz, 1H, ArH); ¹³C NMR (50MHz, CDCl₃) δ 24.22, 26.28, 37.37, 53.49, 101.96, 115.60, 116.03, 117.36, 119.30, 121.95, 125.02, 126.53, 126.75, 130.39, 130.56, 132.71, 136.11, 136.18, 140.33, 150.50, 154.99, 160.40, 165.32.

4-(4-Methoxyphenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3e)
White solid; yield 82%; mp 202-204 °C; FAB MS 380 (M⁺+1); IR (KBr) 2210 cm⁻¹ (CN); ¹H NMR (600 MHz, CDCl₃) δ 1.62-1.65 (m, 2H, CH₂), 1.79-1.83 (m, 4H, 2CH₂), 3.21-3.24 (m, 4H, 2CH₂), 3.91 (s, 3H, OCH₃), 4.10 (s, 2H, CH₂), 6.74 (s, 2H, ArH), 6.89 (d, J = 7.8Hz, 1H, ArH), 6.98-7.05 (m, 2H, ArH), 7.13-7.18 (m, 1H, ArH), 7.34 (d, J = 8.4Hz, 2H, ArH), 7.47 (d, J = 7.2Hz, 1H, ArH).

2-(Piperidin-1-yl)-4-(thiophen-2-yl)-9H-fluorene-1-carbonitrile (3f)
White solid; yield 84%; mp 148-150 °C; FAB MS 357 (M^+1); IR (KBr) 2215 cm⁻¹ (CN); ^1H NMR (200 MHz, CDCl₃) δ 1.60-1.64 (m, 2H, CH₂), 1.79-1.82 (m, 4H, 2CH₂), 3.20-3.25 (m, 4H, 2CH₂), 4.10 (s, 2H, CH₂), 6.92 (s, 1H, ArH), 7.05-7.24 (m, 5H, ArH & 2CH), 7.49-7.54 (m, 2H, ArH & CH); ^13C NMR (50MHz, CDCl₃) δ 24.20, 26.28, 37.37, 53.45, 102.60, 117.29, 120.53, 122.12, 124.93, 126.46, 126.71, 127.23, 127.57, 133.82, 134.49, 140.34, 140.60, 142.28, 150.44, 150.98, 152.31, 154.68; HRMS calcd. for C₂₃H₂₀N₂S 356.13472, Found 356.13580.

4-(Furan-2-yl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3g)
White solid; yield 83%; mp 160-162 °C; ESIMS 341 (M^+1); IR (KBr) 2218 cm⁻¹ (CN); ^1H NMR (300 MHz, CDCl₃) δ 1.58-1.67 (m, 2H, CH₂), 1.76-1.86 (m, 4H, 2CH₂), 3.22-3.27 (m, 4H, 2CH₂), 4.07 (s, 2H, CH₂), 6.60-6.64 (m, 1H, CH), 6.68-6.71 (m, 1H, CH), 7.03 (s, 1H, ArH), 7.19-7.30 (m, 2H, ArH), 7.37-7.43 (m, 1H, ArH), 7.51-7.55 (m, 1H, ArH), 7.64-7.65 (m, 1H, CH); ^13C NMR (50MHz, CDCl₃) δ 24.19, 26.25, 37.47, 53.43, 102.71, 109.88, 111.82, 117.24, 118.48, 122.31, 124.84, 126.74, 126.96, 130.24, 132.98, 140.10, 142.31, 142.79, 150.98, 154.91; HRMS calcd. for C₂₃H₂₀N₂O 340.1576 found 340.1578.

4-(4-Chlorophenyl)-2-(pyrrolidin-1-yl)-9H-fluorene-1-carbonitrile (3h)
White solid; yield 76%; mp 197-199 °C; FAB MS 370 (M+); IR (KBr) 2217 cm⁻¹ (CN); ^1H NMR (600 MHz, CDCl₃) δ 2.00-2.22 (m, 4H, 2CH₂), 3.60-3.80 (m, 4H, 2CH₂), 4.01 (s, 2H, CH₂), 6.36 (s, 1H, ArH), 6.71 (d, J = 7.8Hz, 1H, ArH), 7.00 (t, J = 7.5Hz, 1H, ArH), 7.11 (t, J = 7.5Hz, 1H, ArH), 7.35 (d, J = 8.4Hz, 2H, ArH), 7.42-7.46 (m, 3H, ArH); ^13C NMR (50MHz, CDCl₃) δ 21.47, 25.87, 30.02, 50.14, 91.08, 114.99, 119.89, 121.26, 124.61, 125.19, 126.49, 128.17, 128.57, 129.31, 137.53, 137.95, 141.36, 141.68, 142.73, 148.60, 151.65.

2-(Pyrrolidin-1-yl)-4-p-tolyl-9H-fluorene-1-carbonitrile (3i)
White solid; yield 72%; mp 182-184 °C; ESIMS 351 (M^+1); IR (KBr) 2205 cm⁻¹ (CN); ^1H NMR (200 MHz, CDCl₃) δ 1.99-2.06 (m, 4H, 2CH₂), 2.48 (s, 3H, CH₃), 3.63-3.72 (m, 4H, 2CH₂), 4.03 (s, 2H, CH₂), 6.45 (s, 1H, ArH), 6.80 (d, J = 7.6Hz, 1H, ArH), 7.03-7.18 (m, 2H, ArH), 7.27-7.36 (m, 4H, ArH), 7.47 (d, J = 7.0Hz, 1H, ArH).

4-(4-Acetylphenyl)-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (3j)
White solid; yield 76%; mp 182-184 °C; ESIMS 393 (M^+1); IR (KBr) 1681 (CO), 2213 cm⁻¹ (CN); ^1H NMR (200 MHz, CDCl₃) δ 1.60-1.65 (m, 2H, CH₂), 1.79-1.83 (m, 4H, 2CH₂), 2.71 (s, 3H, CH₃), 3.22-3.26 (m, 4H, 2CH₂), 4.10 (s, 2H, CH₂), 6.78-6.83 (m, 2H, ArH), 7.01-7.10 (m, 1H, ArH), 7.18-7.26 (m, 1H, ArH), 7.50-7.60 (m, 3H, ArH), 8.11 (d, J = 8.0Hz, 2H, ArH); ^13C NMR (50MHz, CDCl₃) δ 24.17, 26.25, 26.88, 37.37, 53.44, 102.27,
White solid; yield 79%; mp 224-226 °C; ESIMS 416 (M⁺+1); IR (KBr) 2211 cm⁻¹ (CN); ¹H NMR (200 MHz, CDCl₃) δ 1.60-1.66 (m, 2H, CH₂), 1.79-1.82 (m, 4H, 2CH₂), 3.22-3.30 (m, 4H, 2CH₂). 4.10 (s, 2H, CH₂), 6.42 (m, 2H, CH), 6.82 (s, 1H, ArH), 6.93 (d, J = 7.8Hz, 1H, ArH), 7.07 (t, J = 7.5Hz, 1H, ArH), 7.17-7.24 (m, 4H, ArH & CH), 7.46-7.59 (m, 4H, ArH).

**General Procedure for the synthesis of compounds 6a-c:** A mixture of 6-aryl-4-sec.-amino-2-oxo-2H-pyran-3-carbonitrile 4a-c (1 mmol), 1-indanone 2 (1.2 mmol) and NaH (2 mmol) in dry THF (5 mL) in N₂ was stirred at room temperature for 5-15 min. The excess THF was removed under vacuum and the reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl. The solid thus obtained was filtered and purified on a silica gel column using 1% ethylacetate in hexane as eluent.

**3-(Piperidin-1-yl)-1-(thiophen-2-yl)-9H-fluorene-4-carbonitrile (6a)**

Yellowish solid; yield 82%; mp 152-154 °C; ESIMS 357 (M⁺+1); IR (KBr) 2217 cm⁻¹ (CN); ¹H NMR (600 MHz, CDCl₃) δ 1.62-1.66 (m, 2H, CH₂), 1.84-1.87 (m, 4H, 2CH₂), 3.20-3.25 (m, 4H, 2CH₂). 3.80 (s, 2H, CH₂), 6.83 (s, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.34-7.38 (m, 1H, ArH), 7.43-7.47 (m, 4H, ArH), 8.5 (d, J = 7.8Hz, 1H, ArH); HRMS calcd. for C₂₃H₂₀N₂S 356.1347 found 356.1139.

**1-(4-Fluorophenyl)-3-(piperidin-1-yl)-9H-fluorene-4-carbonitrile (6b)**

Yellow solid; yield 80%; mp 176-178 °C; FAB MS 368 (M⁺); IR (KBr) 2220 (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.65-1.67 (m, 2H, CH₂), 1.87-1.90 (m, 4H, 2CH₂), 3.21-3.24 (m, 4H, 2CH₂). 3.80 (s, 2H, CH₂), 6.83 (s, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.34-7.38 (m, 1H, ArH), 7.43-7.47 (m, 4H, ArH), 8.55 (d, J = 7.8Hz, 1H, ArH); HRMS calcd. for C₂₅H₂₁FN₂ 368.16888, Found 368.16806.

**1-(2,5-Dimethylfuran-3-yl)-3-(piperidin-1-yl)-9H-fluorene-4-carbonitrile (6c)**

White solid; yield 75%; mp 140-141 °C; ESIMS 369 (M⁺+1); IR (KBr) 2216 cm⁻¹ (CN); ¹H NMR (200 MHz, CDCl₃) δ 1.58-1.62 (m, 4H, 2CH₂), 1.80-1.85 (m, 4H, 2CH₂), 2.32 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 3.15-3.21 (m, 4H, 2CH₂), 3.77 (s, 2H, CH₂), 6.14 (s, 1H, ArH), 6.84 (s, 1H, ArH), 7.33-7.57 (m, 3H, ArH), 8.55 (d, J = 7.2Hz, 1H, ArH).

**General procedure for the synthesis of compounds 7, 8, 9, 10a-h, 11a-b:** A mixture of mixture of fluorene (1 mmol), NaH (1.2 mmol) in THF (5 mL) was stirred at room temperature for 5-15 min. Excess solvent was removed under pressure thereafter the reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl.
HCl. The solid thus obtained was filtered and purified on a silica gel column using 2% ethylacetate in hexane as eluent.

**9H-Fluoren-9-one (7)**

Yellow solid; yield 78%; mp 81-82 °C; ESIMS 181 (M^+1); IR (KBr) 1712 cm^{-1} (CO); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.20-7.30 (m, 2H, ArH), 7.39-7.52 (m, 4H, ArH), 7.60-7.67 (m, 2H, ArH); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 120.30, 124.26, 129.05, 134.66.

**2-Acetyl-9H-fluoren-9-one (8)**

Yellow solid; yield 81%; mp 154-156 °C; ESIMS 223 (M^+1); IR (KBr) 1668 & 1709 cm\(^{-1}\) (CO); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 2.64 (s, 3H, CH\(_3\)), 7.34-7.43 (m, 1H, ArH), 7.51-7.76 (m, 4H, ArH), 8.13-8.22 (m, 1H, ArH); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 27.08, 120.80, 121.65, 124.49, 125.01, 130.61, 134.70, 135.27, 135.41, 138.23, 143.63, 148.83, 193.04, 196.91.

**Anthracene-9,10-dione (9)**

Red solid; yield 76%; mp >250 °C; ESIMS 208 (M^+1); IR (KBr) 1707 cm\(^{-1}\) (CO); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.80-7.86 (m, 4H, ArH), 8.30-8.37 (m, 4H, ArH).

**9-Oxo-2-(pyrrolidin-1-yl)-4-p-tolyl-9H-fluorene-1-carbonitrile (10a)**

Red solid; yield 73%; mp 200-202 °C; ESIMS 365 (M^+1); IR (KBr) 1716 (CO), 2214 cm\(^{-1}\) (CN); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 1.97-2.10 (m, 4H, 2CH\(_2\)), 2.47 (s, 3H, CH\(_3\)), 6.50-6.57 (m, 2H, ArH), 7.07-7.13 (m, 2H, ArH), 7.27-7.32 (m, 4H, ArH), 7.56-7.63 (m, 1H, ArH).

**9-Oxo-2-(piperidin-1-yl)-4-p-tolyl-9H-fluorene-1-carbonitrile (10b)**

Red solid; yield 80%; mp 230-232 °C; ESIMS 379 (M^+1); IR (KBr) 1710 (CO), 2223 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.63-1.67 (m, 2H, CH\(_2\)), 1.74-1.85 (m, 4H, 2CH\(_2\)), 3.19-3.25 (m, 4H, 2CH\(_2\)), 6.61-6.67 (m, 1H, ArH), 6.84 (m, 1H, ArH), 7.14-7.19 (m, 2H, ArH), 7.28-7.33 (m, 4H, ArH), 7.63-7.67 (m, 1H, ArH); HRMS calcd. for C\(_{26}\)H\(_{22}\)N\(_2\)O found 378.1728.

**4-(4-Bromophenyl)-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (10c)**

Red solid; yield 48%; mp >230 °C; MS (ESI) 443 (M^+1); IR (KBr) 1715 (CO), 2221 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.63-1.67 (m, 2H, CH\(_2\)), 1.74-1.85 (m, 4H, 2CH\(_2\)), 3.19-3.25 (m, 4H, 2CH\(_2\)), 6.61-6.67 (m, 1H, ArH), 6.84 (m, 1H, ArH), 7.14-7.23 (m, 2H, ArH), 7.28-7.36 (m, 2H, ArH), 7.64-7.70 (m, 3H, ArH); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 24.00, 26.10, 53.29, 100.78, 114.73, 122.30, 123.26, 124.93, 125.08, 128.61, 130.25, 132.28, 133.85, 134.04, 135.07, 137.66, 141.18, 143.12, 157.14, 190.39.

**9-Oxo-4-phenyl-2-(pyrrolidin-1-yl)-9H-fluorene-1-carbonitrile (10d)**
4-(4-Methoxyphenyl)-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (10e)

Red solid; yield 88%; mp 210-212 °C; FAB MS 395 (M+); IR (KBr) 2210 (CN), 1708 cm⁻¹ (CO); ¹H NMR (200 MHz, CDCl₃) δ 1.60-1.65 (m, 2H, CH₂), 1.77-1.81 (m, 4H, 2CH₂), 3.19-3.26 (m, 4H, 2CH₂), 6.56-6.62 (m, 1H, ArH), 6.85 (s, 1H, ArH), 7.15-7.23 (m, 4H, ArH), 7.37-7.46 (m, 2H, ArH), 7.64-7.69 (m, 1H, ArH); HRMS calcd. for C₂₆H₂₂N₂O₂ 394.1481 found 394.1471.

4-(4-Fluorophenyl)-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (10f)

Red solid; yield 84%; mp 152-154 °C; ESIMS 383 (M⁺+1); IR (KBr) 1713 (CO), 2218 cm⁻¹ (CN); ¹H NMR (200 MHz, CDCl₃) δ 1.59-1.69 (m, 2H, CH₂), 1.78-1.87 (m, 4H, 2CH₂), 3.19-3.26 (m, 4H, 2CH₂), 6.52-6.62 (m, 1H, ArH), 6.82 (s, 1H, ArH), 7.00 (d, J = 8.6 Hz, 2H, ArH), 7.12-7.19 (m, 2H, ArH), 7.32 (d, J = 8.6 Hz, 2H, ArH), 7.62-7.67 (m, 1H, ArH); HRMS calcd. for C₂₅H₁₉FN₂O 382.1481 found 382.1471.

4-(Furan-2-yl)-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile (10g)

Red solid; yield 72%; mp 182-184 °C; ESIMS 355 (M⁺+1); IR (KBr) 1713 (CO), 2220 cm⁻¹ (CN); ¹H NMR (200 MHz, CDCl₃) δ 1.59-1.65 (m, 2H, CH₂), 1.78-1.82 (m, 4H, 2CH₂), 3.19-3.26 (m, 4H, 2CH₂), 6.48-6.54 (m, 2H, CH), 7.00 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.26-7.38 (m, 3H, ArH & CH), 7.64-7.72 (m, 2H, Ar & CH).

9-Oxo-2-(piperidin-1-yl)-4-(thiophen-2-yl)-9H-fluorene-1-carbonitrile (10h)

Yellow solid; yield 76%; mp 226-228 °C; ESIMS 371 (M⁺+1); IR (KBr) 1711 cm⁻¹ (CO), 2220 (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.59-1.69 (m, 2H, CH₂), 1.78-1.87 (m, 4H, 2CH₂), 3.23-3.28 (m, 4H, 2CH₂), 6.83-6.88 (m, 1H, CH), 7.00 (s, 1H, ArH), 7.18-7.26 (m, 4H, ArH), 7.50-7.55 (m, 1H, CH), 7.67-7.71 (m, 1H, CH); HRMS calcd. for C₂₃H₁₈N₂OS 370.1140 found 370.1164.

9-Oxo-3-(piperidin-1-yl)-1-(thiophen-2-yl)-9H-fluorene-4-carbonitrile (11a)

Yellow solid; yield 89%; mp 172-174 °C; ESIMS 371 (M⁺+1); IR (KBr) 1703 (CO), 2218 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.66-1.75 (m, 2H, CH₂), 1.81-1.90 (m, 4H, 2CH₂), 3.38-3.44 (m, 4H, 2CH₂), 6.88 (s, 1H, ArH), 7.15-7.20 (m, 1H, CH), 7.39-7.46 (m, 1H, ArH), 7.47-7.50 (m, 1H, CH), 7.54-7.62 (m, 1H, ArH), 7.68 (d, J = 7.2 Hz, 1H, ArH), 7.82-7.86 (m, 1H, CH), 8.38 (d, J = 7.5 Hz, 1H, ArH).

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1-(4-Fluorophenyl)-9-oxo-3-(piperidin-1-yl)-9H-fluorene-4-carbonitrile (11b)
Yellow solid; yield 91%; mp 180-182 °C; ESIMS 383 (M^+1); IR (KBr) 1707 cm^-1 (CO), 2219 (CN); ^1H NMR (300 MHz, CDCl_3) δ 1.69-1.75 (m, 2H, CH_2), 1.80-1.89 (m, 4H, 2CH_2), 3.39-3.44 (m, 4H, 2CH_2), 6.63 (s, 1H, ArH), 7.16 (t, J = 8.6Hz, 2H, ArH), 7.39-7.53 (m, 3H, ArH), 7.56-7.65 (m, 2H, ArH), 8.37 (d, J = 7.6Hz, 1H, ArH).

General procedure for the synthesis of 12a-c: A mixture of substituted 4-phenyl-2-(sec.amino-1-yl)-9H-fluorene-1-carbonitrile (3a-c) and KOH in DMF was stirred at room temperature for 8-10 minutes. After that reaction mixture was poured into ice water, with vigoursly stirring, the solid thus obtained was filtered and purified on a silica gel column using 1% ethylacetate in hexane as the eluent.

1-Amino-4-(4-bromophenyl)-2-(piperidin-1-yl)-9H-fluoren-9-one (12a)
Red solid; yield 37%; mp 152-154 °C; MS (ESI) 433 (M^+1); IR (KBr) 1671 (CO), 3365 & 3473 cm^-1 (NH_2); ^1H NMR (300 MHz, CDCl_3) δ 1.56-1.60 (m, 2H, CH_2), 1.67-1.78 (m, 4H, 2CH_2), 2.80-2.89 (m, 4H, 2CH_2), 5.99 (bs, 2H, NH_2), 6.71 (s, 1H, ArH), 6.76-6.85 (m, 1H, ArH), 7.10-7.18 (m, 2H, ArH), 7.29-7.35 (m, 2H, ArH), 7.55-7.61 (m, 3H, ArH); ^13C NMR (75 MHz, CDCl_3) δ 24.34, 26.79, 52.99, 115.17, 121.72, 122.57, 123.29, 126.12, 126.93, 127.85, 131.20, 131.79, 133.34, 134.81, 135.98, 139.38, 142.90, 142.94, 143.47, 194.81.

Crystal Data: The crystal data of 12a C_{24}H_{21}BrN_2O, M = 433.34, monoclinic, C2/c, a = 13.1860(1) Å, b = 16.562(2) Å, c = 19.2141(1) Å, β = 103.27(1)°, V = 4084.0(6) Å³, Z = 8, D_c = 1.410 gcm^-3, μ (Mo-Kα) = 2.030 mm^-1, F(000) = 1776, rectangular block, colourless, size = 0.25 x 0.3 x 0.125 mm, 3238 reflections measured (R_int = 0.0426), 1703 unique, wR_2 = 0.1706 for all data, conventional R = 0.0557 [(Δ/σ)max = 000] on F-values of 2523 reflections with I>2σ(I), S = 0.0960 for all data and 254 parameters. Unit cell determination and intensity data collection (2θ = 50°) was performed on a Bruker P4 diffractometer at 293(2) K. Structure solutions by direct methods and refinements by full-matrix least-squares methods on F^2.

1-Amino-2-(piperidin-1-yl)-4-p-tolyl-9H-fluoren-9-one (12b)
Red solid; yield 22%; mp 152-154 °C; MS (ESI) 369 (M^+1); IR (KBr) 1677 (CO), 3353 & 3454 cm^-1 (NH_2); ^1H NMR (200 MHz, CDCl_3) δ 1.68-1.75 (m, 6H, 3CH_2), 2.45 (s, 3H, CH_3), 2.78-2.88 (m, 4H, 2CH_2), 5.97 (bs, 2H, NH_2), 6.76 (s, 1H, ArH), 6.81-6.87 (m, 1H, ArH), 7.08-7.15 (m, 2H, ArH), 7.26-7.36 (m, 4H, ArH), 7.54-7.61 (m, 1H, ArH); HRMS Calcd. for C_{25}H_{25}N_2O 369.19669 and found 369.19633 (M^+H).

1-Amino-4-phenyl-2-(piperidin-1-yl)-9H-fluoren-9-one (12c)
Red solid; yield 25%; mp 152-154 °C; MS (ESI) 355 (M^+1); IR (KBr) 1677 (CO), 3357 & 3448 cm^{-1} (NH_2); ^1H NMR (200 MHz, CDCl_3) δ 1.59-1.62 (m, 2H, CH_2), 1.68-1.79 (m, 4H, 2CH_2), 2.84-2.87 (m, 4H, 2CH_2), 5.97 (bs, 2H, NH_2), 6.75-6.82 (m, 2H, ArH), 7.08-7.14 (m, 2H, ArH), 7.42-7.50 (m, 5H, ArH), 7.55-7.61 (m, 1H, ArH).

**General procedure for the synthesis of 13 & 14:** To a fluorene-1-carboxylic acid (210mg, 1mmol) in dry DCM (15ml) was added chlorosulfanyl isocyanate (0.10 ml, 1.2mmol) during 5 min at 0°C, and the mixture was then stirred at 20°C for 15h. Triethylamine (1.2 mmol) was then added at 0°C over 5 min, and the resulting mixture was stirred for 3hr at room temperature. The reaction mixture was poured into ice water and the product was extracted with CH_2Cl_2 and purified on a silica gel column using 4% ethylacetate in hexane as eluent as 1-cyanofluorene (13). Thus stirring an equimolar mixture of 1-cyanofluorene (13) and KOH in DMF at room temperature, reaction monitored by TLC, at the end reaction mixture poured into ice water and neutralized with dil. HCL, solid thus obtained was filtered and purified on a silica gel column chromatography using 2% ethylacetate as eluent.

**9H-fluorene-1-carbonitrile (13)**
White solid; mp 93-94 °C; ESIMS 192 (M^+1); IR 2221 cm^{-1} (CN).

**9-Oxo-9H-fluorene-1-carbonitrile (14)**
Orange solid; yield 59%; mp 172-174 °C; ESIMS 206 (M^+1); IR (KBr) 1712 (CO) & 2228 cm^{-1} (CN); ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.46 (m, 1H, ArH), 7.51-7.66 (m, 4H, ArH), 7.72-7.78 (m, 2H, ArH).

**General procedure for the synthesis of compounds 17a-b:** A mixture of 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile 16a-b (1 mmol), 2-indanone 2 (1.2 mmol) and NaH (2 mmol) in dry THF (5 mL) in N_2 was stirred at room temperature for 2-5 min. The excess THF was removed under vacuum and there after reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl. The solid thus obtained was filtered and purified on a silica gel column using 2% ethylacetate in hexane as eluent.

**4-(4-Bromophenyl)-2-(methylthio)-9H-fluorene-1-carbonitrile (17a)**
White solid; yield 68%; mp 186-188 °C; ESIMS 391 (M^+1); IR (KBr) 2211 cm^{-1} (CN); ^1H NMR (300 MHz, CDCl_3) δ 2.60 (s, 3H, SCH_3), 4.10 (s, 2H, CH_2), 6.88-6.95 (m, 1H, ArH), 7.07-7.17 (m, 2H, ArH), 7.24-7.38 (m, 3H, ArH), 7.50-7.59 (m, 1H, ArH), 7.63-7.73 (m, 2H, ArH).

**4-(4-Chlorophenyl)-2-(methylthio)-9H-fluorene-1-carbonitrile (17b)**
White solid; yield 63%; mp 188-190 °C; ESIMS 347 (M^+1); IR (KBr) 2214 cm^{-1} (CN); ^1H NMR (300 MHz, CDCl_3) δ 2.60 (s, 3H, SCH_3), 4.09 (s, 2H, CH_2), 6.90 (d, J = 7.86Hz, 1H,
ArH), 7.10-7.16 (m, 2H, ArH), 7.28-7.32 (m, 1H, ArH), 7.39 (d, J = 8.43Hz, 2H, ArH), 7.49-7.55 (m, 3H, ArH); \(^{13}\)C NMR (75MHz, CDCl\(_3\)) \(\delta\) 16.55, 37.06, 108.26, 115.84, 122.70, 125.25, 127.03, 127.16, 127.71, 129.23, 130.15, 134.81, 137.14, 137.85, 139.68, 140.42, 140.60, 142.49, 149.82.

**General procedure for the synthesis of 18a-b:** Similar to the synthesis of 12a-c.

**4-(4-Bromophenyl)-2-(methylthio)-9-oxo-9H-fluorene-1-carbonitrile (18a)**

Yellow solid; yield 43%; mp 244-246 °C; ESIMS 396 (M\(^{+}\)+1); IR (KBr) 1712 (CO), 2214 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.58 (s, 3H, SCH\(_3\)), 6.70 (s, 1H, ArH), 7.14-7.29 (m, 2H, ArH), 7.38-7.69 (m, 6H, ArH).

**4-(4-Chlorophenyl)-2-(methylthio)-9-oxo-9H-fluorene-1-carbonitrile (18b)**

Yellow solid; yield 32%; mp 206-207 °C; ESIMS 362 (M\(^{+}\)+1); IR (KBr) 1716 (CO), 2224 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.60 (s, 3H, SCH\(_3\)), 6.68-6.73 (m, 1H, ArH), 7.17 (s, 1H, ArH), 7.23-7.29 (m, 2H, ArH), 7.44 (d, J = 8.4Hz, 2H, ArH), 7.56 (d, J = 8.4Hz, 2H, ArH), 7.65-7.70 (m, 1H, ArH).

**General procedure for the synthesis 19 & 20:** A mixture of 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2H-pyran-3-carbonitrile 16a (1mmol) and N,N-dimethylamine (1.2 mmol) was refluxed in THF. The crude product obtained was filtered and purified through column chromatography using chloroform as eluent (19). Then 6-(4-bromophenyl)-4-(dimethylamino)-2-oxo-2H-pyran-3-carbonitrile (19) (1 mmol), 2-indanone 2 (1.2 mmol) and (2 mmol) NaH in dry THF was stirred for six min., excess THF was evaporated under vacuum and reaction mixture was poured into ice water, on neutralize with dil. HCL, the solid obtained was filtered and on purification through column chromatography afforded 20.

**6-(4-Bromophenyl)-4-(dimethylamino)-2-oxo-2H-pyran-3-carbonitrile 19**

White solid; yield 72%; mp 212-214 °C; MS (ESI) 318 (M\(^{+}\)+1); IR (KBr) 1701 (CO), 2211 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.45 (s, 6H, 2CH\(_3\)), 6.41 (s, 1H, ArH), 7.61 (d, J = 8.7Hz, 2H, ArH), 7.68 (d, J = 8.7Hz, 2H, ArH).

**4-(4-Bromophenyl)-2-(dimethylamino)-9H-fluorene-1-carbonitrile 20**

White solid; yield 74%; mp 204-206 °C; MS (ESI) 389 (M\(^{+}\)+1); IR (KBr) 2217 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.14 (s, 6H, 2CH\(_3\)), 4.06 (s, 2H, 2CH\(_2\)), 6.65 (s, 1H, ArH), 6.83 (d, J = 7.71Hz, 1H, ArH), 7.08 (t, J = 7.5Hz, 1H, ArH), 7.20 (t, J = 7.3Hz, 1H, ArH), 7.34 (d, J = 8.19Hz, 2H, ArH), 7.51 (d, J = 7.38Hz, 1H, ArH), 7.65 (d, J = 8.19Hz, 1H, ArH).

**General procedure for the synthesis of 21 & 22:** similar procedure as used for 12a-c.

**1-Amino-4-(4-bromophenyl)-2-(dimethylamino)-9H-fluoren-9-one 21**
Red solid; yield 16%; mp 190-192 °C; ESIMS 393 (M^+1); IR (KBr) 1669 (CO), 3366 & 3473 cm\(^{-1}\) (NH\(_2\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 2.70 (s, 6H, 2CH\(_3\)), 6.01 (bs, 2H, NH\(_2\)), 6.73 (s, 1H, ArH), 7.12-7.18 (m, 2H, ArH), 7.32 (d, \(J = 8.3\)Hz, 2H, ArH), 7.56-7.61 (m, 3H, ArH).

4-(4-Bromophenyl)-2-(dimethylamino)-9-oxo-9H-fluorene-1-carbonitrile 22
Red solid; yield 30%; mp 214-216 °C; ESIMS 403 (M^+1); IR (KBr) 1712 (CO), 2220 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.12 (s, 6H, 2CH\(_3\)), 6.55-6.60 (m, 1H, ArH), 6.74 (s, 1H, ArH), 7.11-7.22 (m, 2H, ArH), 7.29-7.34 (m, 2H, ArH), 7.61-7.68 (m, 3H, ArH).

General procedure for the synthesis of 24, 25 and 26: procedure used for the synthesis of 24 is same as 3a-k and procedure used for the preparation of 25 & 26 is same as 12a-c.

4-Isopropyl-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile 24
White solid; yield 80%; mp 144-146 °C; ESIMS 317 (M\(^+\)); IR (KBr) 2215 cm\(^{-1}\) (CN); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.35-1.41 (m, 6H, 2CH\(_3\)), 1.59-1.69 (m, 2H, CH\(_2\)), 1.79-1.85 (m, 4H, 2CH\(_2\)), 3.22-3.27 (m, 4H, 2CH\(_2\)), 3.70-3.85 (m, 1H, CH), 4.02 (s, 2H, CH\(_2\)), 6.93 (s, 1H, ArH), 7.23-7.30 (m, 1H, ArH), 7.37 (t, \(J = 7.29\)Hz, 1H, ArH), 7.55 (d, \(J = 7.26\)Hz, 1H, ArH), 7.83 (d, \(J = 7.74\)Hz, 1H, ArH).

1-Amino-4-isopropyl-2-(piperidin-1-yl)-9H-fluoren-9-one 25
Red solid; yield 28%; mp 144-145 °C; ESIMS 321 (M\(^+\)); IR (KBr) 1676 (CO), 3339 & 3442 cm\(^{-1}\) (NH\(_2\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.31 (d, \(J = 10.2\)Hz, 6H, 2CH\(_3\)), 1.69-1.79 (m, 6H, 3CH\(_2\)), 2.78-2.91 (m, 4H, 2CH\(_2\)), 3.45-3.60 (m, 1H, CH), 5.87 (bs, 2H, NH\(_2\)), 6.89 (s, 1H, ArH), 7.15-7.24 (m, 1H, ArH), 7.35-7.45 (m, 1H, ArH), 7.59-7.64 (m, 2H, ArH).

4-Isopropyl-9-oxo-2-(piperidin-1-yl)-9H-fluorene-1-carbonitrile 26
Red solid; yield 40%; mp 196-198 °C; ESIMS 331 (M\(^+\)); IR (KBr) 1676 (CO), 3339 & 3442 cm\(^{-1}\) (NH\(_2\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.37 (d, \(J = 10.23\)Hz, 6H, 2CH\(_3\)), 1.59-1.65 (m, 2H, CH\(_2\)), 1.75-1.81 (m, 4H, 2CH\(_2\)), 3.17-3.26 (m, 4H, 2CH\(_2\)), 3.48-3.64 (m, 1H, CH), 6.99 (s, 1H, ArH), 7.21-7.29 (m, 1H, ArH), 7.43-7.52 (m, 1H, ArH), 7.55-7.60 (m, 1H, ArH), 7.67-7.72 (m, 1H, ArH).

4.1.5 References


Chapter 4.2

Donor-Acceptor Fluorenes and Fluorenones and their Optical Properties
Chapter 4.2: Donor-Acceptor Fluorenes and Fluorenones and their Optical Properties.

4.2.1 Introduction

Small organic light emitting diode (OLED) displays such as displays of mobile phones, mp3 players, and car radios are on the verge of establishing themselves in the market with great potential to expand in the near future. For full-color flat-panel displays, three primary colors, red, green, and blue, with equal performance are required. Several green and red light emitting organic molecules are commercially available; however, substances suitable for long-term use as blue light emitters are still far from the standards of color purity and thermal stability. Numerous tailor-made mono-, oligo-, or polyfluorenes have proven their potential for preparing blue organic light emitting diodes (B-OLEDs) with high quantum efficiencies, but the scope of their commercialization suffers from the appearance of an additional undesirable low energy “green emission band” (so-called g-band) during device operation, covering a broad range from 500 to 600 nm, which not only reduces the emission efficiency but also destroys the blue color purity. The mechanism of the origin of the “g-band” has been controversial, and debates still continue. There is compelling evidence based on the experiments on fluorene-fluorenone systems that suggests that the oxidation of fluorene to fluorenone is responsible for the emergence of this specific band. In order to avoid oxidation at position 9 of fluorenes, several 9,9-dialkylated fluorenes and spirofluorenes were prepared by blocking the reactive methylene moiety of fluorenes, but they are also found to be vulnerable to photo- or electrooxidative degradation leading to emission band broadening and/or with low electron-hole recombination efficiency. Holmes et al. recently demonstrated that it is possible to prepare oxidatively stable polyfluorenes by carefully prefixing the dialkyl substitution at position 9 of fluorenes. In this chapter, we describe a novel strategy which demonstrates that 9-unsubstituted small molecule fluorenes can be stable bright blue light emitters providing that fluorene/fluorenone systems are “appropriately functionalized” with donor-acceptor and chromophoric groups.

Based on important literature reports on the electrooptical properties of fluorenes, we envisaged that an optimistic strategy is to equip the scaffold with donor-acceptor (D-A) and chromophoric \( \pi \)-groups for controlling emission characteristics, morphological stability, and/or electron-hole recombination efficiency. Despite a large number of synthetic efforts and studies on the fluorene system, to our surprise, only limited synthetic methodologies are available in the literature to architect the fluorene framework. In most of the reports,
commercially available fluorene has been used as a crucial precursor for preparing mono-, oligo-, or polyfluorenes, which offers very limited options for substituent variations.\textsuperscript{18,19} This prompted us to develop new convenient synthesis of donor-acceptor fluorenes and fluorenones with a variety of functional groups.

In order to understand the ‘Green Emission Defect’ in fluorene-based blue OLEDs, following prototype compounds I-IV were prepared and evaluated for their optical properties.

![Chemical Structures](image)

**Figure 1.**

### 4.2.2 Chemistry

#### 4.2.2.1 Synthesis of substituted 1-phenyl-3-(amin-1-yl)-9H-fluorene-4-carbonitrile (3a-e) and substituted 9-oxo-1-phenyl-3-(amin-1-yl)-9H-fluorene-4-carbonitrile (4a-e): Our approach to preparing 1,3,4-functionalized fluorenes (3a-e) was based on the ring transformation of 6-aryl-2H-pyran-2-ones (1a-e) by using 1-indanone (2) as a carbanion source. The 2H-pyran-2-ones (1a-e) used as a parent precursors were conveniently prepared by the reaction of methyl 2-cyano-3,3-dimethylsulfanylacrylate\textsuperscript{20} with substituted acetophenones under alkaline conditions in high yields, followed by reaction with secondary amines. The C-6 position of lactones, 1a-e is highly susceptible to nucleophilic attack due to the extended conjugation and the presence of the electron withdrawing substituent at position 3 of the pyranone ring. The transformation of 6-aryl-2H-pyran-2-ones into fluorenes is possibly initiated by attack of the carbanion generated from 1-indanone at position C-6 of lactone (1a-e), followed by intramolecular cyclization involving the carbonyl functionality of 2 and C-3 of the pyranone ring and elimination of carbon dioxide, followed by protonation and dehydration afforded 3a-e in good yields. The synthesis of 1,3,4-functionalized fluorene compounds (3a-e) was achieved by stirring an 1:1.2 molar mixture of 2H-pyran-2-ones (1a-e), 1-indanone (2) and (2 molar) NaH in dry THF for 5-8 min. in N\textsubscript{2} atmosphere at room temperature (Scheme 1).
Our Approach to prepare substituted 9-oxo-1-phenyl-3-(amin-1-yl)-9H-fluorene-4-
carbonitrile (4a-e) was based on the oxidation of substituted 1-phenyl-3-(amin-1-yl)-9H-
fluorene-4-carbonitrile (3a-e) with NaH in THF. The synthesis of fluorenones 4a-e was
achieved by stirring an equimolar mixture of 3a-e and NaH in THF for 5-10 min. (Scheme 1).

All the synthesized compounds were characterized by their spectroscopic analysis. IR
spectrum of one of the compounds 3a showed a band at 2203 cm\(^{-1}\) due to a CN group. Two
multiplets were appeared at \(\delta\) 2.01-2.05 ppm and 3.68-3.72 ppm for 4H each assigned to
pyrrolidine protons. One singlet at \(\delta\) 3.78 ppm for 2H was assigned to methylene protons.
One singlet, one multiplet and one doublet at \(\delta\) 6.63, 7.30-7.51 and 8.63 ppm for one proton,
eight protons and one protons were assigned to aromatic protons, respectively. The mass
spectrum (ESIMS) at \(m/z\) 337 together with HRMS analysis confirmed the structure of the
compound 3a as 1-phenyl-3-(pyrrolidin-1-yl)-9H-fluorene-4-carbonitrile.
Chapter 4.2

\(^1\)H NMR spectrum of fluorenone 4a showed two multiplets at \(\delta\) 2.05-2.07 and 3.77-3.81 ppm for 4H each was assigned to pyrrolidine protons. One singlet, one multiplet and one doublet at \(\delta\) 6.35 ppm for 1H, 7.31-7.60 ppm for 8H and 8.39 ppm for 1H were assigned to aromatic protons. IR spectrum showed peaks at 1695 (CO) and 2206 (CN) cm\(^{-1}\) due to presence of a carboxyl and a cyano group. Mass spectrum (ESIMS) 351 (M\(^++\)1) together with HRMS confirms the structure as 9-oxo-1-phenyl-3-(pyrrolidin-1-yl)-9H-fluorene-4-carbonitrile 4a (figure 2).

Figure 2 \(^1\)H and \(^{13}\)C NMR spectra of 1-phenyl-3-(pyrrolidin-1-yl)-9H-fluorene-4-carbonitrile 3a

Figure 3 \(^1\)H and \(^{13}\)C NMR spectra of 9-oxo-1-phenyl-3-(pyrrolidin-1-yl)-9H-fluorene-4-carbonitrile 4a.

4.2.2.2 Synthesis of substituted 4-phenyl-2-(amin-1-yl)-9H-fluorene-1-carbonitrile (6a-e) and substituted 9-oxo-4-phenyl-2-(amin-1-yl)-9H-fluorene-1-carbonitrile (7a-e): Our approach to preparing 1,2,4-functionalized fluorenes (6a-e) was based on the ring transformation of 6-aryl-2H-pyran-2-ones (1a-e) by using 2-indanone (5) as a carbanion source. The synthesis of 1,2,4-functionalized fluorene compounds (6a-e) was achieved by
stirring an 1:1.2 molar mixture of 2H-pyran-2-ones (1a-e), 2-indanone (5) and 2 molar NaH in dry THF for 5-8 min. in N₂ atmosphere at room temperature (Scheme 2).

Our Approach to prepare 9-oxo-4-phenyl-2-(amin-1-yl)-9H-fluorene-1-carbonitrile (7a-e) was based on the oxidation of fluorenes (6a-e). A simple stirring of 4-phenyl-2-(amin-1-yl)-9H-fluorene-1-carbonitrile (6a-e) and NaH in THF, for 5-10min. afforded 7a-e in good yields (Scheme 2). All the synthesized compounds were characterized by spectroscopic analysis.

<table>
<thead>
<tr>
<th>entry</th>
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<th>Amine</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>a</td>
<td>phenyl</td>
<td>pyrrolidine</td>
<td>90</td>
</tr>
<tr>
<td>b</td>
<td>phenyl</td>
<td>piperidine</td>
<td>89</td>
</tr>
<tr>
<td>c</td>
<td>1-naphthyl</td>
<td>piperidine</td>
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</tr>
<tr>
<td>d</td>
<td>2-naphthyl</td>
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<td>87</td>
</tr>
<tr>
<td>e</td>
<td>1-pyrenyl</td>
<td>piperidine</td>
<td>90</td>
</tr>
</tbody>
</table>

Scheme 2

The ¹H NMR of the compound 6a showed two multiplets at δ 1.99-2.08 and 3.65-3.73 ppm for pyrrolidine protons. Two singlets at δ 4.04 and 6.47 ppm for methylene protons and one aromatic proton. One doublet, two triplets and one multiplet at δ 6.72, 7.01, 7.13 and 7.41-7.52 for nine aromatic protons were in agreement with the proposed structure. The presence of the cyano peak at 1707 cm⁻¹ in IR spectrum and the molecular ion peak m/z at 336 in the mass spectrum confirmed the structure as 4-phenyl-2-(pyrrolidin-1-yl)-9H-fluorene-1-carbonitrile 6a (Figure 4).

The ¹H NMR of the compound 7a showed two multiplets at δ 1.97-2.10 and 3.67-3.73 ppm for pyrrolidine protons. One singlet at δ 6.59 ppm and five multiplets at δ 6.43-6.48, 7.04-7.12, 7.40-7.47, 7.48-7.54 and 7.55-7.59 for ten aromatic protons were in agreement with the proposed structure. The presence of the carbonyl peak at 1717 and cyano peak at 2215 cm⁻¹ in IR spectrum and the molecular ion peak m/z at 351 in the mass spectrum confirmed the structure as 9-oxo-4-phenyl-2-(pyrrolidin-1-yl)-9H-fluorene-1-carbonitrile 7a (Figure 5).
4.2.3 Optical properties of synthesized compounds 3a-e, 4a-e, 6a-e and 7a-e: The synthesized fluorenes and fluorenones were treated as small molecules with properly functionalized Donor-acceptor and chromophoric groups. A systematic study including UV-vis, Fluorescence, Thermal properties, Cyclic Voltammetry and finally device fabrication was done to evaluate the effectiveness of our molecules, to acts as stable blue light emitting molecules (BOLEDs).

4.2.3.1 UV-Vis and Fluorescence (photoluminescence) spectrum of 3a-e, 4a-e, 6a-e and 7a-e: The photophysical properties of all of the synthesized compounds 3a-e, 4a-e, 6a-e, and 7a-e were examined by UV-Vis and photoluminescence techniques. UV/Vis spectra were obtained with Thermo Electron–Nicolet evolution-5000 spectrometer with slit width of 1.5, using THF as solvent of choice having concentration is 1 µM. Photoluminescence spectra were obtained with Varian-Cary eclipse C-100 with slit width of 1.5, using THF as solvent of choice, having concentration is 1 µM. Figure 6 represents the UV-graphs and normalized photoluminescence graphs of all synthesized fluorenes (3a-e, 6a-e) and fluorenones (4a-e, 7a-e).
7a-e). Maximum absorbance, emission wavelength, color of emission and stokes shift together with optical band gap ($E_{opt}$) calculated from absorption edge is summarised in Table 1.
Figure 6. Showing UV-Vis and normalized Fluorescence spectra of fluorenes (3a-e, 6a-e) and fluorenones (4a-e, 7a-e).

Table 1. Photophysical properties of fluorenes (3a-e, 6a-e) and fluorenones (4a-e, 7a-e).

<table>
<thead>
<tr>
<th>compd</th>
<th>$\lambda_{\text{max, abs}}$ (nm)</th>
<th>$\lambda_{\text{max, em}}$ (nm)</th>
<th>Stokke's shift (cm$^{-1}$)</th>
<th>$E_{\text{op}}$ (eV)</th>
<th>PL color</th>
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<tr>
<td>3a</td>
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<td>446</td>
<td>5900</td>
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<tr>
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<td>528</td>
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<td>7a</td>
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<td>-</td>
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<td>7b</td>
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<td>460</td>
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<td>7d</td>
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<tr>
<td>7e</td>
<td>344</td>
<td>473</td>
<td>7930</td>
<td>3.38</td>
<td>B</td>
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</tbody>
</table>

*Longest wavelength absorption maximum. *Molar extinction co-efficients, *Fluorescence emission maximum, *Stokes shift = (1/\$\lambda_{\text{abs}}$ - 1/\$\lambda_{\text{em}}$), *Color of the emitted light, B (blue), GY (greenish yellow), NF means no fluorescence.

The structure-property relationships of a series of fluorenes and fluorenones revealed that the absorption maxima did not increase with the number of condensed rings increased at the position 1 in fluorenes 3a-e. A blue shift (14 nm) was observed in the case of pyrene (3e: 147
346 nm) as a chromophore compare to phenyl group (3b: 360 nm). Such a blue shift disappear in the case of respective fluorenones (4b and 4e) where the difference in absorption maxima is only one nm (4b: 392 nm; 4e: 393 nm). In the case of fluorenones 7a, 7b and 7d, they do not show the fluorescence. However, fluorenones 7e and 7e show blue fluorescence. In general high intensity absorption occurred in the case of pyrene ($E_{\text{max}}$: 6e, 7170, 7e, 6510) as a chromophore, which indicated that transition is accompanied by a large change in the dipole moment of transition, and thus a large change in the electronic charge distribution occurred during excitation. The emission maxima for the fluorene 6e (481 nm) is remarkably red shifted (32 nm) compare to corresponding phenyl-substituted fluorene (6b: 449 nm). The stoke’s shift, which reflects the difference in the energy of the excitation and emission spectra was found to be higher for pyrene in a same series (3,4 and 6,7). Thus we selected fluorenes (3e, 4e) and fluorenones (6e, 7e) for detailed studies.

4.2.3.2 Calculation of Quantum yields of 3e, 4e, 6e and 7e: The procedure for determining the fluorescence quantum yield follows established techniques. The quantum yield is determined as mentioned below:

$$\phi_c = \phi_s \frac{(\text{AUC})_c \times (\text{OD})_c \times n^2_c}{(\text{AUC})_s \times (\text{OD})_s \times n^2_s}$$

Where subscripts c and s refers to compound and standard, respectively. AUC = Area under curve. OD = optical density. Concentration of compounds was 6.67 X 10^{-7} M, solution in THF.

Yields were calculated by taking Harmine as standard. The quantum yield of Harmine is 0.450.

<table>
<thead>
<tr>
<th>Code</th>
<th>Absorbance</th>
<th>Integrated intensity</th>
<th>$\phi_c$</th>
</tr>
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<td>6e</td>
<td>0.032</td>
<td>804.7897</td>
<td>0.405</td>
</tr>
<tr>
<td>7e</td>
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<td>380.5438</td>
<td>0.201</td>
</tr>
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<td>1200.3503</td>
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<tr>
<td>10e</td>
<td>0.043</td>
<td>440.4205</td>
<td>0.389</td>
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4.2.3.3 Thermal Properties of 3e, 4e, 6e and 7e: Thermal properties of fluorenes (3e, 6e) and fluorenones (4e, 7e) were investigated using Perkin-Elmer TG/DTA analyser. Graphs were presented in Figure 7. Compound 6e exhibited good thermal stability. It showed less than 10% decomposition upto 300°C under nitrogen and lost about 20% weight at 440°C.
Figure 7. Thermal graphs of 3e, 4e, 6e and 7e

<table>
<thead>
<tr>
<th>Temperature (Td)</th>
<th>Td&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Td&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>3e</td>
<td>183</td>
<td>212</td>
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<tr>
<td>6e</td>
<td>300</td>
<td>440</td>
</tr>
<tr>
<td>4e</td>
<td>359</td>
<td>516</td>
</tr>
<tr>
<td>7e</td>
<td>310</td>
<td>363</td>
</tr>
</tbody>
</table>

<sup>a</sup>decomposition temperature at 10% weight loss.
<sup>b</sup>decomposition temperature at 20% weight loss.

4.2.3.4 Time decay and semi-empirical calculations: The geometries of the fluorenes in the ground state were optimized with the semi-empirical Austin Model (AM1)<sup>31</sup> method. Figure 8 inset shows the frontier orbital diagram of 6e based on AM1 calculation. The geometrically optimized structure of 6e shows pyrene ring to be oriented almost perpendicular to the molecular plane of the fluorene with the piperidine and cyano substituents. From the frontier orbital diagram, it is evident that the HOMO has the charge.
density localized on the pyrenyl moiety. The excited state LUMO doesn’t show any significant change in the \( \pi \)-electron distribution but in the higher excited state LUMO+1, the electron density distribution is on the fluorene ring extending to the cyano group and to the nitrogen atom of the piperidine moiety suggesting that these moieties definitely play an important role in the PL features.

To probe the photoluminescence mechanism of these fluorenes, we carried out nanosecond time decay measurements\(^\text{22}\) for the fluorene 6e. The life time decay traces of the integrated PL between 400 and 600 nm were measured in solid state as shown in Fig 8. The time resolved PL (TRPL) decay of the compound is fitted to a tri-exponential decay model with a time constant of \( \tau_1 = 1.3 \), \( \tau_2 = 3.7 \) and \( \tau_3 = 7.4 \) ns. The tri-exponential decay component arises predominantly from the pyrene, fluorene and CN moieties as evident from the semi-empirical calculation. The fact that majority of the excited states indicate a localized electron density on the pyrene moiety suggest that the slow decay component \( \tau_3 = 7.4 \) ns of TRPL curve and the predominant blue PL component arises from the pyrenyl part of the component. This is because in the above three excited states, the pyrene moiety have 66% delocalization of electrons compared to 33% delocalization in the fluorene moiety along with the cyano linkage. Therefore the faster decay component \( \tau_2 \) & \( \tau_1 \) appears to come from \(-C=N\) and fluorene moieties respectively. The blue PL may be mainly due to the transition from HOMO to LUMO+2 levels. The dipole moment and the total energy of the molecule 6e are found to be 3.6137 D and 0.25134388 au respectively, from AM1 calculations.

![Graph](image_url)

Figure 8. Time decay measurement and AM1 Calculation of 6e for HOMO and LUMO

4.2.3.5 Cyclic Voltammogram plot of 6e: The electrochemical studies\(^\text{23}\) were carried out using EPSILON series CV instrument. Cyclic voltammetric measurements were performed in dichloromethane using Standard calomel electrode (SCE) as standard electrode and Pt as
the working electrode in 0.001M-tetra butyl ammonium perchlorate electrolytic conditions as described in the literature to ascertain the redox behavior of the compounds and the HOMO–LUMO energy values. The energy of the HOMO of the 6e compound is determined according to the equation, \([-E_{\text{oxd}} - 4.8]\) eV where \(E_{\text{oxd}}\) is the potential at the onset of oxidation. The HOMO was estimated to be \(-5.8\) eV from the oxidation onset potential. The corresponding LUMO level was calculated based on the optical band gap of 3.2 eV. The LUMO value was estimated to be \(-2.6\) eV.

![Cyclic voltammogram of 6e](image)

**Figure 9.** Cyclic voltammogram of 6e

### 4.2.3.6 Device Fabrication and Electroluminescent studies:

In order to investigate the electrochemical behaviours multilayers devices were fabricated for 3e and 6e. All the organic layers were deposited by vacuum sublimation onto patterned, pre-cleaned and ozone treated indium tin oxide (ITO) collated glass substrates. The entire fabrication was carried out in Hind high Vac nitrogen box equipped with thermal evaporation assembly. A hole injecting PEDOT: PSS (Baytron P 8000) layer was spin coated to a thickness of 40nm and vacuum dried. TPD as a hole transport layer was evaporated on the follow through up to30nm. The model compound 3e or 6e was deposited up to 50-60nm and was sandwiched between TPD and an electron transport material such as BCP (8nm). A thin layer of LiF (high band gap insulator) was topped on to BCP layer. Aluminium layer was finally deposited as the cathodic material. The following layer structure was prepared and tested: ITO/PEDOT:PSS/TPD (30nm)/3e or 6e (60nm)/BCP(8nm)/LiF(0.5nm)/Al (160 nm).

### 4.2.4. Result and Discussion

The photophysical properties of all of the synthesized compounds 3a-e, 4a-e, 6a-e, and 7a-e were examined by UV-vis and photoluminescence techniques (Table 1). All of the fluorenes (3a-e) substituted at position 1 with different chromophoric groups (π-groups) such
as phenyl, naphthyl, or pyrenyl showed PL in the blue region (3a-e, $\lambda_{PL}$ 442-462 nm), while their corresponding fluorenones (4a-e) showed PL in the yellowish green region (4a-e, $\lambda_{PL}$ 526-529 nm). When we changed the positions of these donor-acceptor and chromophoric groups as shown in a series of fluorenes 6a-e, all fluorenes exhibited PL in the blue region (6a-e, $\lambda_{PL}$ 446-481 nm) but their corresponding fluorenones showed either blue PL (7c: $\lambda_{PL}$ 460 nm, 7e: $\lambda_{PL}$ 473 nm) or no PL (7a, b, d) depending on the chromophores attached at position 4 on the fluorenone scaffold. Our approach to demonstrate GED is shown in Figure 10 taking pyrenylfluorenes (3e, 6e) and pyrenylfluorenones (4e, 7e) as representative compounds. Figure 10 revealed that yellowish green light emitting fluorenone 4e ($\lambda_{max}$ 528 nm) can be converted to blue light emitting fluorenone 7e ($\lambda_{max}$ 473 nm) by rearranging the substitution pattern on the fluorenone scaffold. Based on emission spectra of 3e, 4e, 6e, and 7e, it may be predicted that the device made up of 3e may in principle show GED because its corresponding fluorenone 4e showed PL in the yellowish green region, while the device made up of 6e as emissive layer should be free from GED because its corresponding fluorenone 7e showed PL in the blue region. In other words, preparing an OLED with a small molecule such as 4-pyrenyl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile 6e, where both fluorene (6e, $\lambda_{max}$ 481 nm) and the corresponding fluorenone (7e, $\lambda_{max}$ 473 nm) showed PL in the blue region, should retain blue color purity in the OLED device (Figure 10).

In order to validate our novel approach for inhibiting the defect, fluorenes 3e and 6e were selected for fabrication of an OLED device to understand the GED phenomenon. The cyclic voltammogram of 6e showed one fully reversible oxidation wave at +1.14 V, corresponding to a one-electron acceptor process, providing scope as a good hole transporting material (Figure 9).

To validate our concept of swapping the donor-acceptor sites in the fluorene framework, we employed the compounds 3e and 6e separately as an emissive layer in a multilayer OLED. The following layer structure was prepared and tested: ITO/PEDOT:PSS/TPD (30nm)/3e or 6e (60nm)/BCP(8nm)/ LiF(0.5nm)/Al (160 nm). The EL characteristics of both compounds are shown in Figure 11. EL of compound 6e showed a sharp peak at 476 nm with a fwhm of 60 nm, and that of 3e exhibited a peak at 489 nm with fwhm of 120 nm. The $\lambda_{max}$ of PL (solution) of 6e agrees well with the EL spectrum, while a red shift of 29 nm is observed in EL of 3e. The broad and low intensity emission band in 3e appears to be coming from the oxidation of fluorene 3e to fluorenone 4e during device operation, which is also in agreement with the photoluminescence studies performed by mixing fluorenes (3e or 6e) and their corresponding fluorenones (4e or 7e) in varying weight
fractions (Figure 12). To further evaluate the electrochemical stability of fluorenes 3e and 6e, the EL spectra of these fluorenes were recorded with increase in applied voltage at an interval of 1 V. The shift in wavelength of 3e and 6e is plotted in Figure 13. A remarkable red shift is observed in the device of 3e with an increase in the applied voltage, while the device 6e was found to be stable even under bias stress. This shows the effectiveness of the model 6e in containing the emission of the blue region. The degradation of 3e at applied voltage >9 V shows the formation of fluorenone responsible for green emission defect and a bathochromic shift.

Figure 10. GED Phenomenon: Normalized PL spectra of fluorene (3e, 6e) and fluorenone (4e, 7e) in THF. Inset: emission color variability produced by these compounds. Colored arrows indicate either a red shift or a blue shift in PL.

Figure 11. Normalized EL spectra of 3e and 6e at 5V. Inset: Device Configuration of 3e and 6e.
Figure 12. Comparative study of (3e & 4e) and (6e & 7e)

Figure 13. I-L-V characteristic of Device 3e and 6e, pictures of 3e and 6e and Plot of EL wavelength as a function of voltage for the device made with 3e and 6e compounds.

The current density-voltage and luminance-voltage characteristics of device 3e and 6e are plotted in the inset of Figure 13. The current efficiency of both the molecules is shown in the Figure 14. The device made of 6e is more efficient than the device made of 3e under similar processing conditions and device structure. Despite an overall device thickness of about ~100 nm, the device for the 6e compound shows substantially low (3.5 V) “ON” voltage with good luminescence efficiency (0.85 Cd/A) and good brightness as shown in the inset of Figure 14. At a luminescence density of 572.5 Cd/m², the efficiency is still 0.61 Cd/A (Figure 14). The (x,y) coordinates of emission color produced by 3e and 6e are (0.23, 0.37) and (0.16, 0.26), respectively, in the chromaticity graphs. The compound 6e gives more saturated and bright color in comparison to 3e and also remains comparatively stable during the device operation as evident from Figures 13 and 14. The stable blue color clearly confirms the role of appropriately swapped donor-acceptor moieties in the fluorene ring.
4.2.5 Conclusion

We described an elegant and highly rapid methodology for novel series of donor-acceptor fluorenes and fluorenones in excellent yields. We also demonstrated a novel strategy to improve blue color purity by shifting the fluorenone emission band from the "green region" to the "blue region" by appropriate positioning of donor-acceptor and chromophoric groups onto the fluorene/fluorenone backbone. The photoluminescent and electroluminescent studies of 4-pyrenyl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile 6e revealed stable blue emission with a low turn on voltage of 3.5V and a brightness of 573 Cd/m² with good chemical, thermal, and electrochemical stability. Our concept of swapping donoracceptor and chromophores on the fluorene scaffold at appropriate positions would offer futuristic approaches toward both synthetic and device performance and more importantly to improve blue color purity of fluorene-based OLEDs for paving the way for commercialization.

4.2.6 Experimental Section

General procedure for the synthesis of 3a-e and 6a-e: A mixture of 1 (1 mmol), 1-indanone 2 or 2-indanone 5 (1 mmol) and sodium hydride (2 mmol) in dry THF (10 mL) was stirred at 5°C to room temperature for less than five minutes (Caution: Long time stirring may result to a mixture with oxidized byproducts). After completion, the reaction solvent was evaporated under vacuum and the crude solid obtained was quenched with ice water and subsequently neutralized by 10% HCl. The precipitate thus obtained was filtered and purified on a silica gel column using ethyl acetate in hexane as eluent.
1-Phenyl-3-pyrrolidin-1-yl-9H-fluorene-4-carbonitrile (3a)

White solid; mp 158-160 °C; ESIMS 337 (M$^{+}$+ 1); IR (KBr) 2203 cm$^{-1}$ (CN); $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 2.01-2.05 (m, 4H, 2CH$_2$), 3.68-3.72 (m, 4H, 2CH$_2$), 3.78 (s, 2H, CH$_2$), 6.63 (s, 1H, ArH), 7.30-7.51 (m, 8H, ArH), 8.63 (d, $J$ = 7.6 Hz, 1H, ArH); $^{13}$C NMR (50.00 MHz, CDCl$_3$) $\delta$ 26.34, 36.10, 51.22, 88.25, 113.65, 120.77, 123.14, 124.97, 127.39, 128.09, 128.39, 128.73, 129.02, 130.73, 140.41, 141.02, 143.89, 145.36, 145.40, 152.35; HRMS calcd. for C$_{24}$H$_{20}$N$_2$ 336.1627 Found 336.1599.

1-Phenyl-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (3b)

White solid; mp 156-156 °C; ESIMS 351 (M$^{+}$+1); IR (KBr) 2214 cm$^{-1}$ (CN); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.61-1.70 (m, 2H, CH$_2$), 1.84-1.92 (m, 4H, 2CH$_2$), 3.19-3.30 (m, 4H, 2CH$_2$), 3.54 (d, 2H, CH$_2$), 7.00 (s, 1H, ArH), 7.33-7.63 (m, 8H, ArH), 7.97 (d, $J$ = 8.12Hz, 2H, ArH), 8.64 (d, $J$ = 7.8Hz, 1H, ArH); $^{13}$C NMR (75.53 MHz, CDCl$_3$) $\delta$ 22.86, 25.03, 34.33, 52.76, 97.13, 116.69, 117.50, 121.36, 123.53, 124.14, 124.34, 124.87, 124.91, 125.22, 125.94, 127.00, 127.19, 127.25, 129.68, 132.40, 135.37, 136.53, 138.21, 141.05, 143.26, 143.37, 156.43; HRMS (ESIMS) calcd. for C$_{29}$H$_{24}$N$_2$ 401.2017 Found 401.2018.

1-Naphthalen-1-yl-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (3c)

White solid; mp 188-190 °C; ESIMS 401 (M$^{+}$+1); IR (KBr) 2214 cm$^{-1}$ (CN); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.60-1.69 (m, 2H, CH$_2$), 1.83-1.92 (m, 4H, 2CH$_2$), 3.19-3.30 (m, 4H, 2CH$_2$), 3.54 (d, 2H, CH$_2$), 7.00 (s, 1H, ArH), 7.33-7.63 (m, 8H, ArH), 7.97 (d, $J$ = 8.12Hz, 2H, ArH), 8.64 (d, $J$ = 7.8Hz, 1H, ArH); $^{13}$C NMR (75.53 MHz, CDCl$_3$) $\delta$ 22.86, 25.03, 34.33, 52.76, 97.13, 116.69, 117.50, 121.36, 123.53, 124.14, 124.34, 124.87, 124.91, 125.22, 125.94, 127.00, 127.19, 127.25, 129.68, 132.40, 135.37, 136.53, 138.21, 141.05, 143.26, 143.37, 156.43; HRMS (ESIMS) calcd. for C$_{29}$H$_{24}$N$_2$ 401.2017 Found 401.2018.

1-Naphthalen-2-yl-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (3d)

White solid; mp 136-138 °C; ESIMS 401 (M$^{+}$+1); IR (KBr) 2214 cm$^{-1}$ (CN); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.61-1.70 (m, 2H, CH$_2$), 1.84-1.92 (m, 4H, 2CH$_2$), 3.24-3.29 (m, 4H, 2CH$_2$), 3.92 (s, 2H, CH$_2$), 7.06 (s, 1H, ArH), 7.37-7.68 (m, 6H, ArH), 7.91-8.06 (m, 4H, ArH), 8.63 (d, $J$ = 7.8 Hz, 1H, ArH); $^{13}$C NMR (50.00 MHz, CDCl$_3$) $\delta$ 24.59, 26.74, 36.45, 54.46, 98.69, 118.23, 118.38, 123.05, 125.15, 126.68, 126.98, 127.07, 127.65, 127.84, 128.22, 128.60, 128.69, 128.79, 133.30, 133.75, 135.58, 138.03, 139.80, 143.82, 145.02, 145.45, 158.18; HRMS calcd. for C$_{29}$H$_{24}$N$_2$ 400.1940 Found 400.1939.

3-Piperidin-1-yl-1-pyren-1-yl-9H-fluorene-4-carbonitrile (3e)
White solid; mp 114-116 °C; ESIMS 475 (M°+1); IR (KBr) 2215 cm⁻¹ (CN); ¹H NMR (300 Hz, CDCl₃) δ 1.60-1.69 (m, 2H, CH₂), 1.84-1.93 (m, 4H, 2CH₂), 3.25-3.31 (m, 4H, 2CH₂), 3.56 (s, 2H, CH₂), 7.12 (s, 1H, ArH), 7.35-7.38 (m, 2H, ArH), 7.45-7.54 (m, 1H, ArH), 7.77-7.83 (m, 1H, ArH), 7.96-8.10 (m, 3H, ArH), 8.16-8.23 (m, 3H, ArH), 8.28 (t, J = 7.5 Hz, 2H, ArH), 8.67 (d, J = 7.8 Hz, 1H, ArH); ¹³C NMR (50.00 MHz, CDCl₃) δ 24.57, 26.76, 36.24, 54.48, 98.88, 118.47, 119.52, 123.13, 125.14, 125.26, 125.76, 126.02, 126.73, 126.95, 127.68, 127.70, 128.36, 128.52, 128.65, 128.75, 131.29, 131.63, 131.81; HRMS (ESIMS) calcd. for C₁₃H₂₆N₂ 474.2096 Found 474.2091.

4-Phenyl-2-pyrrolidin-1-yl-9H-fluorene-1-carbonitrile (6a)
White solid; mp 210-212 °C; MS (FAB) 336 (M⁺); IR (KBr) 2208 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.99-2.08 (m, 4H, 2CH₂), 3.65-3.73 (m, 4H, 2CH₂), 4.04 (s, 2H, CH₂), 6.47 (s, 1H, ArH), 6.72 (d, J = 7.8 Hz, 1H, ArH), 7.01 (t, J = 7.6 Hz, 1H, ArH), 7.13 (t, J = 7.6 Hz, 1H, ArH), 7.41-7.52 (m, 6H, ArH); ¹³C NMR (75.53 Hz, CDCl₃): δ 24.50, 36.66, 48.88, 90.0, 113.64, 118.40, 119.85, 123.28, 123.92, 125.16, 125.79, 126.79, 126.90, 127.27, 127.31, 139.10, 139.87, 140.33, 141.29, 147.16, 150.32; HRMS calcd. for C₂₄H₂₀N₂ 336.1626 Found 336.1623.

4-Phenyl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (6b)
White solid; mp 140-141 °C; ESIMS 351 (M°⁺1); IR (KBr) 2219 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.62-1.75 (m, 2H, CH₂); 1.80-1.88 (m, 4H, 2CH₂), 3.26-3.33 (m, 4H, 2CH₂), 4.10 (s, 2H, CH₂), 6.86-6.91 (m, 2H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.22 (t, J = 7.6 Hz, 1H, ArH), 7.45-7.51 (m, 6H, ArH); ¹³C NMR (75.53 MHz, CDCl₃): δ 22.84, 24.96, 36.00, 52.15, 100.45, 116.08, 117.93, 120.78, 123.54, 125.06, 125.34, 126.97, 127.35, 127.42, 131.32, 138.85, 139.20, 140.94, 141.01, 149.06, 153.62; HRMS (ESIMS) calcd. for C₂₉H₂₄N₂ 351.1861 Found 351.1821.

4-Naphthalen-1-yl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (6c)
White solid; mp 148-149 °C; ESIMS 401 (M⁺⁺1); IR (KBr) 2213 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.62-1.68 (m, 2H, CH₂); 1.80-1.88 (m, 4H, 2CH₂), 3.26-3.33 (m, 4H, 2CH₂), 4.18 (s, 2H, CH₂), 6.14 (d, J = 7.8 Hz, 1H, ArH), 6.84 (t, J = 7.8 Hz, 1H, ArH), 6.96 (s, 1H, ArH), 7.14 (t, J = 7.5 Hz, 1H, ArH), 7.37 (t, J = 7.5 Hz, 1H, ArH), 7.48-7.57 (m, 4H, ArH), 7.61-7.68 (m, 1H, ArH), 7.98-8.08 (m, 2H, ArH); ¹³C NMR (75.53 MHz, CDCl₃): δ 22.84, 24.94, 36.08, 52.16, 100.72, 116.12, 118.56, 120.75, 123.36, 124.30, 124.48, 124.92, 125.0, 125.36, 125.43, 127.09, 127.29, 130.15, 132.29, 132.64, 136.40, 138.86, 138.99, 140.82, 148.79, 153.65; HRMS calcd. for C₂₉H₂₄N₂ 401.1654 Found 401.1635.
4-Naphthalen-2-yl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (6d)

White solid; mp 142-144 °C; ESIMS 401 (M^+1); IR (KBr) 2215 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.62-1.68 (m, 2H, CH₂); 1.79-1.87 (m, 4H, 2CH₂), 3.26-3.32 (m, 4H, 2CH₂), 4.14 (s, 2H, CH₂), 6.86 (d, J = 7.8 Hz, 1H, ArH), 6.93 (s, 1H, ArH), 6.98 (t, J = 7.6 Hz, 1H, ArH), 7.21 (t, J = 7.6 Hz, 1H, ArH), 7.52-7.63 (m, 4H, ArH), 7.89-8.04 (m, 4H, ArH); ¹³C NMR (75.53 MHz, CDCl₃) δ 24.55, 26.63, 37.75, 53.84, 102.20, 117.79, 119.88, 122.57, 125.23, 126.77, 126.95, 127.04, 127.30, 127.80, 128.33, 128.65, 128.69, 133.10, 133.42, 133.82, 138.04, 140.89, 142.57, 142.66, 150.86, 155.36; HRMS (ESIMS) calcd. for C₂₉H₂₄N₂ 401.2017 Found 401.1980.

2-Piperidin-1-yl-4-pyren-1-yl-9H-fluorene-1-carbonitrile (6e)

White solid; mp 168-169 °C; ESIMS 475 (M^+1), IR (KBr) 2217 cm⁻¹ (CN); ¹H NMR (300 MHz, CDCl₃) δ 1.60-1.68 (m, 2H, CH₂), 1.79-1.89 (m, 4H, 2CH₂), 3.28-3.34 (m, 4H, 2CH₂), 4.21 (s, 2H, CH₂), 5.98 (d, J = 7.8 Hz, 1H, ArH), 6.68 (t, J = 7.5 Hz, 1H, ArH), 7.02 (s, 1H, ArH), 7.08 (t, J = 7.5 Hz, 1H, ArH), 7.51 (d, J = 7.5 Hz, 1H, ArH), 7.79 (d, J = 9.2 Hz, 1H, ArH), 7.94 (s, 1H, Ar), 7.96-8.10 (m, 2H, ArH), 8.16-8.22 (m, 3H, ArH), 8.28 (d, J = 7.5 Hz, 1H, ArH), 8.33 (d, J = 7.8 Hz, 1H, ArH); ¹³C NMR (75.53 MHz, CDCl₃) δ 24.54, 26.66, 37.83, 55.88, 102.46, 117.91, 120.68, 122.39, 125.19, 125.24, 125.33, 125.80, 125.93, 126.72, 127.18, 127.89, 128.38, 128.64, 129.16, 131.46, 131.75, 134.48, 135.28, 140.79, 141.03, 142.55, 150.65, 155.33; HRMS calcd. for C₃₅H₂₆N₂ 474.2096 Found 474.2093.

General procedure for the oxidation of fluorenes to fluorenones (4a-e and 7a-e): A solution of fluorenes (3a-e or 6a-e, 1 mmol) in THF (10 mL) was added sodium hydride (2 mmol) and the solution was stirred at 0-25°C for less than five minutes. After completion, the reaction solvent was evaporated under vacuum and the crude solid obtained was quenched with ice water and subsequently neutralized by dilute HCl. The precipitate thus obtained was filtered and purified on a silica gel column using ethyl acetate-hexane as the eluent.

9-Oxo-1-phenyl-3-pyrrolidin-1-yl-9H-fluorene-4-carbonitrile (4a)

Yellow solid; mp 202-204°C; ESIMS 351 (M^+1); IR (KBr) 2206 (CN), 1695 cm⁻¹ (CO); ¹H NMR (300 Hz, CDCl₃) δ 2.05-2.07 (m, 4H, 2CH₂), 3.77-3.81 (m, 4H, 2CH₂), 6.35 (s, 1H, ArH), 7.31-7.60 (m, 8H, ArH), 8.39 (d, J = 7.6 Hz, 1H, ArH); ¹³C NMR (50.00 MHz, CDCl₃) δ 25.91, 51.32, 88.81, 115.48, 119.76, 123.78, 123.92, 128.41, 129.32, 130.83,
134.35, 136.11, 137.87, 140.64, 147.18, 152.97, 153.97, 189.70; HRMS calcd. for C24H18N2O 351.1497 Found 351.1461.

9-Oxo-1-phenyl-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (4b)
Yellow solid; mp 166-168 °C; ESIMS 365 (M+1); IR (KBr) 2219 (CN), 1705 cm\(^{-1}\) (CO); \(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.65-1.74 (m, 2H, CH\(_2\)), 1.80-1.89 (m, 4H, 2CH\(_2\)), 3.38-3.44 (m, 4H, 2CH\(_2\)), 6.68 (s, 1H, ArH), 7.41 (t, \(J = 7.5\) Hz, 1H, ArH), 7.45-7.54 (m, 5H, ArH), 7.57-7.59 (m, 1H, ArH), 7.59-7.64 (m, 1H, ArH), 8.37 (d, \(J = 7.5\) Hz, 1H, ArH); \(^13\)C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 22.68, 24.67, 51.55, 95.24, 115.94, 118.11, 120.97, 121.16, 122.41, 126.70, 127.64, 129.33, 133.10, 133.94, 135.61, 139.20, 145.60, 149.61, 158.96, 188.36; HRMS (ESIMS) calcd. for C\(_{24}\)H\(_{18}\)N\(_2\)O 351.1463 Found 351.1462.

1-Naphthalen-1-yl-9-oxo-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (4c)
Yellow solid; mp 180-182 °C; ESIMS 415 (M+1); IR (KBr) 2213 (CN), 1707 cm\(^{-1}\) (CO); \(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.68-1.74 (m, 2H, CH\(_2\)), 1.80-1.89 (m, 4H, 2CH\(_2\)), 3.37-3.47 (m, 4H, 2CH\(_2\)), 6.76 (s, 1H, ArH), 7.35-7.63 (m, 8H, ArH), 7.92-7.99 (m, 2H, ArH), 8.41 (d, \(J = 7.8\) Hz, 1H, ArH); \(^13\)C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 22.65, 24.68, 51.57, 95.45, 115.96, 118.89, 121.27, 122.49, 122.80, 123.78, 123.92, 124.68, 124.78, 125.04, 127.22, 127.57, 129.35, 130.02, 132.05, 133.10, 133.93, 134.13, 139.41, 143.51, 149.06, 158.86, 187.99; HRMS (ESIMS) calcd. for C\(_{29}\)H\(_{22}\)N\(_2\)O 415.1736 Found 415.1735.

1-Naphthalen-2-yl-9-oxo-3-piperidin-1-yl-9H-fluorene-4-carbonitrile (4d)
Yellow solid; mp 166-167 °C; ESIMS 415 (M+1); IR (KBr) 2218 (CN), 1712 cm\(^{-1}\) (CO); \(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.70-1.75 (m, 2H, CH\(_2\)), 1.82-1.91 (m, 4H, 2CH\(_2\)), 3.41-3.47 (m, 4H, 2CH\(_2\)), 6.79 (s, 1H, ArH), 7.43 (t, \(J = 7.5\) Hz, 1H, ArH), 7.50-7.66 (m, 5H, ArH), 7.89-7.98 (m, 4H, ArH), 8.40 (d, \(J = 7.6\) Hz, 1H, ArH); HRMS calcd. for C\(_{29}\)H\(_{22}\)N\(_2\)O 414.1735.

9-Oxo-3-piperidin-1-yl-1-pyren-1-yl-9H-fluorene-4-carbonitrile (4e)
Yellow solid; mp 220-222 °C; MS (EI) 488 (M+); IR (KBr) 2218 (CN), 1708 cm\(^{-1}\) (CO); \(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.67-1.73 (m, 2H, CH\(_2\)), 1.80-1.89 (m, 4H, 2CH\(_2\)), 3.38-3.51 (m, 4H, 2CH\(_2\)), 6.85 (s, 1H, ArH), 7.39 (t, \(J = 7.5\) Hz, 1H, ArH), 7.53 (d, \(J = 7.5\) Hz, 1H, ArH), 7.61 (t, \(J = 7.5\) Hz, 1H, ArH), 7.86-8.10 (m, 4H, ArH), 8.00-8.20 (m, 4H, ArH), 8.25 (t, \(J = 7.4\) Hz, 1H, ArH), 8.44 (d, \(J = 7.7\) Hz, 1H, ArH); \(^13\)C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 24.34, 25.38, 53.27, 97.16, 117.73, 121.16, 123.00, 124.20, 124.50, 124.74, 124.98, 125.24, 125.71, 125.92, 126.51, 127.00, 128.36, 129.10, 131.08, 131.28, 131.80, 131.95, 132.91, 134.83,
9-Oxo-4-phenyl-2-pyrrolidin-1-yl-9H-fluorene-1-carbonitrile (7a)
Light red solid; mp 166-168 °C; ESIMS 351 (M^+1); IR (KBr) 2215 (CN), 1717 cm\(^{-1}\) (CO);
\(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.97-2.10 (m, 4H, CH\(_2\)), 3.67-3.73 (m, 4H, 2CH\(_2\)), 6.43-6.48 (m, 1H, ArH), 6.59 (s, 1H, ArH), 7.04-7.12 (m, 2H, ArH), 7.40-7.47 (m, 2H, ArH), 7.48-7.54 (m, 3H, ArH), 7.55-7.59 (m, 1H, ArH); 13C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 24.50, 49.37, 88.60, 115.58, 119.27, 120.14, 123.11, 126.0, 127.12, 127.33, 127.49, 129.34, 132.13, 133.40, 136.26, 137.69, 141.23, 142.34, 149.32, 189.94.

9-Oxo-4-phenyl-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (7b)
Light red solid; mp 220-222 °C; ESIMS 365 (M^+1); IR (KBr) 2220 (CN), 1709 cm\(^{-1}\) (CO);
\(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.62-1.68 (m, 2H, CH\(_2\)), 1.77-1.87 (m, 4H, 2CH\(_2\)), 3.22-3.26 (m, 4H, 2CH\(_2\)), 6.57-6.65 (m, 1H, ArH), 6.91 (s, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.42-7.46 (m, 2H, ArH), 7.51-7.56 (m, 3H, ArH), 7.64-7.68 (m, 1H, ArH); HRMS (ESIMS) calcd. for C\(_{29}\)H\(_{20}\)N\(_2\)O 365.1654 Found 365.1651.

4-Naphthalen-1-yl-9-oxo-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (7c)
Light red solid; mp 202-204 °C; ESIMS 415 (M^+1); IR (KBr) 2221 (CN), 1719 cm\(^{-1}\) (CO),
\(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.59-1.66 (m, 2H, CH\(_2\)), 1.78-1.87 (m, 4H, 2CH\(_2\)), 3.22-3.28 (m, 4H, 2CH\(_2\)), 5.88 (d, \(J = 7.6\) Hz, 1H, ArH), 6.92 (t, \(J = 7.5\) Hz, 1H, ArH), 7.01 (s, 1H, ArH), 7.05 (t, \(J = 7.5\) Hz, 1H, ArH), 7.39-7.67 (m, 6H, ArH), 7.98-8.10 (m, 2H, ArH); 13C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 24.32, 26.43, 53.65, 101.12, 115.20, 122.68, 124.93, 125.70, 125.99, 126.30, 126.68, 126.99, 127.44, 128.60, 128.97, 129.55, 131.44, 133.99, 134.16, 135.34, 135.92, 136.49, 137.57, 140.78, 143.44, 157.47, 191.00; HRMS calcd. for C\(_{29}\)H\(_{22}\)N\(_2\)O 414.1732 Found 414.1714.

4-Naphthalen-2-yl-9-oxo-2-piperidin-1-yl-9H-fluorene-1-carbonitrile (7d)
Light red solid; mp 182-184 °C; ESIMS 415 (M^+1); IR (KBr) 2213 (CN), 1695 cm\(^{-1}\) (CO),
\(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.60-1.68 (m, 2H, CH\(_2\)), 1.78-1.87 (m, 4H, 2CH\(_2\)), 3.23-3.29 (m, 4H, 2CH\(_2\)), 6.61 (d, \(J = 7.4\) Hz, 1H, ArH), 6.99 (s, 1H, ArH), 7.05-7.20 (m, 2H, ArH), 7.50 (d, \(J = 8.4\) Hz, 1H, ArH), 7.59-7.64 (m, 2H, ArH), 7.68 (d, \(J = 7.8\) Hz, 1H, ArH), 7.90-8.05 (m, 4H, ArH); 13C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 24.34, 26.43, 53.64, 100.90, 115.21, 122.84, 125.10, 125.91, 126.67, 127.33, 127.84, 128.37, 128.65, 128.74, 129.07, 133.58, 133.71, 134.20, 134.69, 135.31, 136.50, 137.87, 142.82, 143.71, 157.47, 190.96.
9-Oxo-2-piperidin-1-yl-4-pyren-1-yl-9H-fluorene-1-carbonitrile (7e)

Light red solid; mp 180-182 °C; ESMS 489 (M^+1); IR (KBr) 2217 (CN), 1713 cm\(^{-1}\) (CO);

\(^1\)H NMR (300 Hz, CDCl\(_3\)) \(\delta\) 1.59-1.66 (m, 2H, CH\(_2\)), 1.79-1.87 (m, 4H, 2CH\(_2\)), 3.26-3.32 (m, 4H, 2CH\(_2\)), 5.74 (d, \(J = 7.6\) Hz, 1H, ArH), 6.78 (t, \(J = 7.5\) Hz, 1H, ArH), 7.0 (t, \(J = 7.5\) Hz, 1H, ArH), 7.10 (s, 1H, ArH), 7.66 (d, \(J = 7.4\) Hz, 1H, ArH), 7.84 (d, \(J = 9.2\) Hz, 1H, ArH), 7.94-8.15 (m, 3H, ArH), 8.18-8.26 (m, 3H, ArH), 8.31-8.40 (m, 2H, ArH); \(^1\)C NMR (75.53 MHz, CDCl\(_3\)) \(\delta\) 24.32, 26.45, 53.67, 115.11, 122.65, 124.73, 124.99, 125.40, 126.06, 126.22, 126.70, 126.86, 126.93, 127.79, 128.66, 128.73, 128.98, 129.11, 131.35, 131.78, 132.08, 133.49, 139.17, 135.40, 136.03, 137.81, 141.30, 143.53, 157.45; HRMS calcd. for C\(_{35}\)H\(_{24}\)N\(_2\)O \(488.1895\) Found 488.1889.

4.2.7 References


